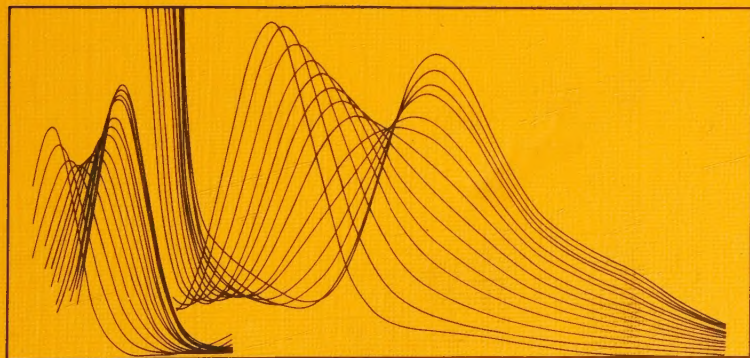


MECHANISMS FOR LIGAND SUBSTITUTIONS IN
PLATINUM(II) AND GOLD(III) SYSTEMS AND
REDOX PROCESSES IN GOLD(III) COMPLEXES

ANN-BRITT GRÖNING



LUND 1979

Mechanisms for Ligand Substitutions in Platinum(II) and
Gold(III) Systems and Redox Processes in Gold(III) Complexes.

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av

Ann-Britt Gröning
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Mechanisms for Ligand Substitutions in Platinum(II) and Gold(III)
Systems and Redox Processes in Gold(III) Complexes.

Referat (sammandrag) Kinetic measurements using stopped-flow and conventional spectrophotometry have been used to elucidate mechanisms for (i) halide substitution processes of chloro-bromo complexes of platinum(II) and of chloro-bromo, chloro-thiocyanato and bromo-thiocyanato complexes of gold(III), (ii) the reactions between the aqua complexes $PtCl_n(H_2O)_{4-n}$, $n=0,1,2,3,4$ (including cis- and trans-isomers for $n=2$) and the entering ligands chloride, bromide, iodide, thiocyanate, dimethyl sulfoxide and ethene and (iii) the reduction of tetrachloro- and tetrabromo aurate(III) by thiocyanate.

Mechanisms for the solvent (k_1) path of substitution processes have been comprehensively studied. The solvent path is much more important for the reactions of the platinum(II) complexes than of the gold(III) complexes. The kinetic evidence speak in favour of an associative mechanism via a bipyramidal intermediate for both the solvent path and the direct substitution.

There is no evidence for participating of longlived five-coordinate intermediates in the ligand substitution reaction of gold(III) which has been proposed. Aqua complexes are shown to react (continued overleaf)

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more rapidly with entering nucleophiles than corresponding parent chloro or bromo complexes in all cases studied, which is also contrary to some previous results.

The empirical parameters that affect the reaction rates, viz. trans-effects, cis-effects, leaving and entering groups and the central metal ion have been systematically studied and quantitatively evaluated (esp. DMSO and ethene).

For the reaction between gold(III) halide and thiocyanate the experiments indicate rapid ligand substitution followed by a slower reductive elimination to gold(I) species via an attack on the gold(III) complex by an outer-sphere thiocyanate. Trace amounts of cyanide formed in the redox step inhibit the reduction.

This review gives a summary of the results from the following papers. They will be referred to by their Roman numerals.

- I L.I. Elding and A-B. Gröning,
Ligand Substitution Reactions of Mixed Chloro-Bromo
Complexes of Platinum(II).
Chemica Scripta 11 (1977) 8.
- II L.I. Elding and A-B. Gröning,
The Solvent Path in Square-Planar Substitutions. Kinetics
and Mechanism for Reactions of Tetrachloroplatinate(II)
and Aquachloroplatinates(II) with Halides, Thiocyanate
and Dimethyl Sulfoxide.
Inorg. Chim. Acta 31 (1978) 243.
- III L.I. Elding and A-B. Gröning,
Solvent paths for Square-Planar Substitutions. Part 2.
Reactions between Aqua Chloroplatinates(II) and Ethene.
Inorg. Chim. Acta, Submitted.
- IV L.I. Elding and A-B. Gröning,
Kinetics, Mechanism and Equilibria for Halide Substitution
Processes of Chloro-Bromo Complexes of Gold(III).
Acta Chem. Scand. A32 (1978) 867.
- V L.I. Elding, A-B. Gröning and Ö. Gröning,
Kinetics and Mechanism for the Reaction between Tetrachloro-
and Tetrabromo Aurate(III) and Thiocyanate

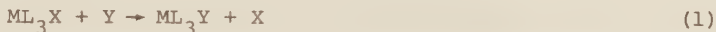
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1. INTRODUCTION

Kinetic studies of ligand substitutions in square-planar complexes have mainly been limited to those of platinum(II) and palladium(II). Information about the behaviour of corresponding gold(III) complexes has appeared only lately in the literature.¹⁻⁶ Several books and reviews present a general account of the field.⁷⁻¹⁶

Experimental rate laws for substitution reactions at square-planar complexes of the type



usually contain two terms

$$\text{rate} = (k_1 + k_2[Y]) [\text{complex}] \quad (2)$$

The constant k_2 characterizes the direct reaction between the complex and the entering ligand Y. It is generally assumed that the intimate mechanism for the k_2 -path is an associative reaction *via* a five-coordinated transition complex between the substrate and Y.

There are many examples of stable five-coordinate complexes of Pt(II), Pd(II) and Au(III) which might serve as models for such transition states. For instance, $Pt(SnCl)_5^{3-}$ has a trigonal bipyramidal structure.¹⁷ Square-planar $Ni(CN)_4^{2-}$ is able to add a fifth cyanide ligand to give $Ni(CN)_5^{3-}$, which occurs in both a trigonal bipyramidal structure and in a square-pyramidal form.¹⁸ All attempts to obtain kinetic evidence for the existence of five-coordinate intermediates in substitution reactions of Pt(II) complexes have failed, however. In the case of Ni(II), Rh(I) and Ir(I) complexes, rate laws indicating the existence of five-coordinate intermediates have been reported.¹⁹⁻²¹ Hall and Satchell have recently postulated the existence of persistent five-coordinate intermediates in some gold(III) substitutions (cf. 1.3).²²

Whether the k_1 -term in the rate law (2) has its origin in an associative reaction with the solvent or in a dissociative process *via* an intermediate with decreased coordination number (cf. Fig.3)

has been thoroughly discussed in the literature.⁷⁻⁹ If the reaction is associative, solvento complexes will appear as intermediates in steady-state concentrations. Obviously, a knowledge of the reactivity of solvento complexes will therefore be of great importance when these mechanisms are discussed. A substantial amount of work dealing with the solvent path has appeared in the literature recently,²²⁻³⁵ but there is still a great deal of confusion concerning the mechanism for this path.

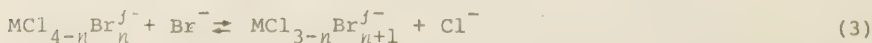
The present study has been devoted to the following three problems (1.1-1.3) in the field of square-planar substitution reactions:

1.1. The k_1 -(or solvent) path.

Studies of the mechanism for the solvent path in aqueous solution are inherently connected with the reactivity of aqua complexes, which are the postulated intermediates in an associative process.

The synthesis of the tetra-aqua platinum(II) ion, $\text{Pt}(\text{H}_2\text{O})_4^{2+}$,³⁶ opened new possibilities in this respect. By starting from the tetra-aqua ion it was possible to prepare several aqua complexes that could serve as intermediates. In a few cases, aqua complexes have been reported to react slowly (or not at all) with entering ligands C_6H_5 . Milburn and Venanzi³⁰, Mureinik³¹ and Bekker and Robb.^{28,32} This is not compatible with other experiments,³⁷⁻⁴¹ which demonstrate rapid reactions between aqua complexes and nucleophiles, and therefore, required a careful investigation. In papers II and III a systematic study of the reactions between the complexes $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$, $n=0,1,2,3,4$ and the entering ligands $\text{Y}=\text{Cl}^-$, Br^- , I^- , SCN^- , DMSO and C_2H_4 is reported.

It was also of interest to compare the relative contributions from the solvent paths to the over-all reactions for various metals. Therefore the stepwise substitutions of chloride by bromide in the gold(III) and platinum(II) tetra-chloro complexes described by eqn (3) were studied ($n=0,1,2,3,4$; $j=1,2$) (I and IV)



Previous quantitative kinetic studies of the stepwise halide exchanges (3) have been mainly restricted to the first step ($n=0$). Louw and Robb⁵ have determined the rate constants for this reaction in aqueous solution for $M=Au(III)$. Cattalini et al^{4,41} have studied the reaction of MCl_4^{f-} with various ligands, among them bromide, thiocyanate and iodide, for $M=Pt(II)$ in aqueous solutions and for $M=Au(III)$ in methanol. The stepwise equilibrium constants for the equilibria (3) have been determined for the $Pt(II)$ system by Dunning and Martin⁴³ using a radiochemical technique, and for $M=Au(III)$ by Almgren⁴⁴ and by Peshchevitskii and Belevantsev⁴⁵ using spectrophotometric measurements and by Pouradier and Coquard⁴⁶ from potentiometric studies.

1.2. Empirical reactivity correlations

It was also of interest to evaluate quantitatively the empirical parameters which can be used to describe the reactivity in square-planar systems *viz.* the nature of the *trans*-ligand, the two *cis*-ligands, the entering and the leaving groups and the central metal ion.

Each of these parameters can be studied by a systematic variation while all the others are held constant. However, the effect of the leaving group, the entering group and the *trans*-ligand are intimately connected with each other in an associative mechanism *via* a trigonal bipyramidal intermediate (cf. the figure on page 35) Also, the ionic charge of the complex influences the reaction rate for charged entering ligands.

Attempts to systematize the rate constants in order to obtain a quantitative description of these empirical effects have been made (I). The rate constants for substitution of water by an entering nucleophile can be described by an empirical equation of the type^{47,48}

$$k/m = \kappa \cdot T \cdot C_1 \cdot C_2 \cdot Q^q \quad (4)$$

where m is a statistical factor (the number of equivalent leaving ligands in the complex), κ is a characteristic for the entering

ligand, the leaving ligand and the central metal ion. T is the relative *trans*-effect for the *trans*-ligand and C_1 and C_2 are the relative *cis*-effects for the two *cis*-ligands. Simple empirical relationships like (4) are valuable, since they summarize a large amount of kinetic information using a few parameters, and since they can be used to predict rate constants for related reactions. They are of course far from the more advanced treatments of the reactivity using MO-theory, which quantum chemists have lately started.^{49,50} A prerequisite for such calculations, however, is systematic experimental information on large series of related reactions.

The choice of thiocyanate as entering ligand was due to the peculiar result for the reaction between SCN^- and $\text{PtCl}_3\text{H}_2\text{O}^-$ reported by Mureinik.³¹ Thiocyanate is a linear ambidentate ligand with approximately equal charges at the sulfur and the nitrogen atoms.⁵¹⁻⁵³ It coordinates via the sulfur to both platinum(II)⁵⁴ and gold(III)⁵⁵ as long as no steric hindrance exists.

It was also desirable to study dimethyl sulfoxide, ethene and thiocyanate as nucleophiles because of their large *trans*-effects. It has been suggested that ligands with large *trans*-effects ususally are good nucleophiles,⁸ and it was therefore interesting to compare these ligands with the halides. DMSO and C_2H_4 form very stable 1:1 complexes with platinum(II). DMSO is a polar molecule with a positive charge at the sulfur atom⁵⁶ and it is coordinated via the sulfur atom to platinum(II)⁵⁷ like thiocyanate. Ethene is a linear symmetrical ligand coordinating to the square planar Pt(II) complexes with its axis perpendicular to the plane⁵⁸ containing the platinum atom and the three other ligands of the complex. The relative importance of σ and π contributions to the bonding between the metal and ethene has been discussed.⁵⁹⁻⁶¹

1.3. Persistent five-coordinate intermediates

Another reason for the extension of this work to include the reaction of AuCl_4^- with bromide (eqn. (3) above) and of AuX_4^- , $\text{X}=\text{Cl}, \text{Br}$, with thiocyanate (V) was the reported evidence for long-

lived five-coordinate intermediates in the substitution reactions between AuCl_4^- and bromide, thiocyanate and iodide, studied by Hall and Satchell.²² As mentioned above, five-coordinate intermediates are mechanistically important in the discussion of square-planar substitutions, and a careful examination of the existence of such intermediates was therefore considered valuable.

2. STOICHIOMETRIC REACTION MODELS, NOTATIONS, AND REVIEW OF REACTIONS

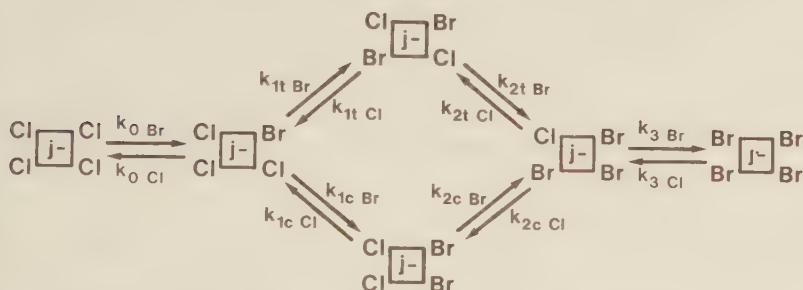
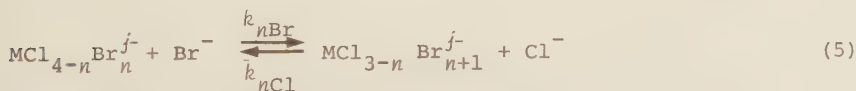


Figure 1. Stoichiometric reaction model for stepwise halide exchanges.

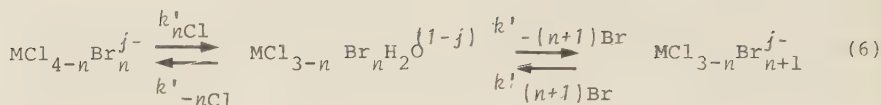
The scheme in Figure 1 is applicable for the direct halide exchanges in platinum(II) (I) as well as for the gold(III)-chloride-bromide, chloride-thiocyanate and bromide-thiocyanate reactions (IV,V). The rate constants $k_{n\text{Br}}$ and $k_{n\text{Cl}}$ are defined according to (5) ($\text{M}=\text{Au}, \text{Pt}; j=1,2$)



where $n=0,1,2,3$, compare scheme (14) on page 23.

The stepwise equilibrium constants are denoted $K_n = k_{n\text{Br}}/k_{n\text{Cl}}$, $n=0,1,2,3$ (I,IV).

The acid hydrolyses and halide anations rate constants are defined by (6) for $\text{M}=\text{Pt}$ (I) and by scheme (14) on page 23 for $\text{M}=\text{Au}$ (IV).



where $n=0,1,2,3$.

The experiments for the reaction between AuX_4^- , $\text{X}=\text{Cl}, \text{Br}$, and thiocyanate (V) indicate rapid ligand substitutions analogous to those in Fig. 1 followed by a slower reductive elimination of Au(III) to Au(I) thiocyanato species, which also has a half-life within the stopped-flow region. The scheme in Figure 2 is applicable for relatively low concentrations of thiocyanate ($[\text{SCN}^-] \leq 5 \text{ mM}$). Since the substitution and reduction are kinetically separated by a factor of 10 to 100 they can be studied independently of each other.

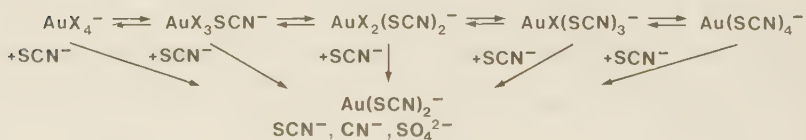


Figure 2. Reaction model for the reaction between gold(III) halide and thiocyanate.

For the reactions studied in papers II and III, the rate constants for the direct reaction of the substrate complex with Y are denoted k_2 . The acid hydrolysis rate constant and the reverse halide anation rate constant are denoted by k_1 and k_{-1} , respectively for all Y. The rate constant for the reaction between the aqua complex formed in the k_1 -path and Y is denoted by k_3 , compare scheme (21), page 25.

All the reactions of the mixed chloro-bromo-complexes of platinum(II) and gold(III) are summarized in Table I. The four substitution reactions (M), (N), (O), (P) studied in (V) are also included in the Table, together with some reactions reported in the literature (Q,X,Y,Ö for M=Au). The statistically corrected values, k/m are also given, c.f. eqn.(4).

Table II gives the rate constants for the reactions studied in papers II and III, together with the values adjusted for the influence of statistical factors and ionic charge, (k/mQ^q) (c.f. page 9).

3. EXPERIMENTAL

All experiments were performed using an aqueous perchloric acid-sodium perchlorate medium of ionic strength 1.00 M, at 25.0°C.

3.1. Preparation of complexes.

Commercially available potassium tetrachloroplatinate(II), K_2PtCl_4 , potassium tetrabromoplatinate(II) dihydrate, $K_2PtBr_4 \cdot 2H_2O$, and hydrogen tetrachloroaurate(III) trihydrate, $HAuCl_4 \cdot 3H_2O$, were used without further purification.

Solutions of tetrabromaurate(III) were prepared by addition of excess sodium bromide to solutions of the tetrachloroaurate(III). (IV,V).

Dilute solutions of the tetraaquaplatinum(II) perchlorate were prepared by addition of excess silver(I) perchlorate to potassium tetrachloroplatinate(II) as described by Elding.³⁶

Solutions of trichloroaquaplatinate(II), $PtCl_3H_2O^-$ and trichloroquaaurate(III), $AuCl_3H_2O$ were prepared similarly by addition of one equivalent of silver(I) perchlorate to solutions of potassium tetrachloroplatinate(II) (II) and hydrogen tetrachloroaurate(III) (IV) and solutions of $PtCl(H_2O)_3^+$ were obtained by addition of one equivalent of silver(I) to solutions

Table I. Rate constants at 25°C, 1.00 M perchlorate medium for reactions of gold(III) and platinum(II) complexes. Ionic charges of the complexes excluded.

Reaction	Rate constant	M = Au		M = Pt		$10^{-6}k_{\text{Au}}/k_{\text{Pt}}$
		$k_{\text{Au}}/\text{M}^{-1}\text{s}^{-1}$	$(k_{\text{Au}}/m)/\text{M}^{-1}\text{s}^{-1}$	$10^5k_{\text{Pt}}/\text{M}^{-1}\text{s}^{-1}$	$10^5(k_{\text{Pt}}/m)/\text{M}^{-1}\text{s}^{-1}$	
<u>Halide Exchanges</u>						
A $\text{MCl}_4 + \text{Br}^-$	$\rightarrow \text{MCl}_3\text{Br} + \text{Cl}^-$	63.3±2.3 (IV)	16	4.8 (I)	1.2	1.3
B $\text{MCl}_3\text{Br} + \text{Br}^-$	$\rightarrow t\text{-MCl}_2\text{Br}_2 + \text{Cl}^-$	240±20 (IV)	240	8.9 (I)	8.9	2.7
C $\text{MCl}_3\text{Br} + \text{Br}^-$	$\rightarrow c\text{-MCl}_2\text{Br}_2 + \text{Cl}^-$	29 (IV)	14.5	2.6 (I)	1.3	1.1
D $t\text{-MCl}_2\text{Br}_2 + \text{Br}^-$	$\rightarrow \text{MClBr}_3 + \text{Cl}^-$	29.5±1.5 (IV)	14.8	0.94 (I)	0.47	3.1
E $c\text{-MCl}_2\text{Br}_2 + \text{Br}^-$	$\rightarrow \text{MClBr}_3 + \text{Cl}^-$	456±40 (IV)	228	10.0 (I)	5.0	4.6
F $\text{MClBr}_3 + \text{Br}^-$	$\rightarrow \text{MBr}_4 + \text{Cl}^-$	185±13 (IV)	185	2.8 (I)	2.8	5.8
G $\text{MCl}_3\text{Br} + \text{Cl}^-$	$\rightarrow \text{MCl}_4 + \text{Br}^-$	0.26±0.03 (IV)	0.26	0.45 (I)	0.45	0.056
H $t\text{-MCl}_2\text{Br}_2 + \text{Cl}^-$	$\rightarrow \text{MCl}_3\text{Br} + \text{Br}^-$	7.0 (IV)	3.5	4.2 (I)	2.1	0.13
I $c\text{-MCl}_2\text{Br}_2 + \text{Cl}^-$	$\rightarrow \text{MCl}_3\text{Br} + \text{Br}^-$	0.45 (IV)	0.23	0.60 (I)	0.30	0.075
J $\text{MClBr}_3 + \text{Cl}^-$	$\rightarrow t\text{-MCl}_2\text{Br}_2 + \text{Br}^-$	0.19 (IV)	0.19	0.15 (I)	0.15	0.113
K $\text{MClBr}_3 + \text{Cl}^-$	$\rightarrow c\text{-MCl}_2\text{Br}_2 + \text{Br}^-$	6.2 (IV)	6.2	3.1 (I)	1.55	0.174
L $\text{MBr}_4 + \text{Cl}^-$	$\rightarrow \text{MClBr}_3 + \text{Br}^-$	10.7±2.5 (IV)	2.7	3.0 (I)	0.8	0.38
M $\text{MCl}_4 + \text{SCN}^-$	$\rightarrow \text{MCl}_3\text{SCN} + \text{Cl}^-$	$1.3 \cdot 10^4$ (V)	$3.3 \cdot 10^3$	(1.00±0.06)·10 ³ (III)	$2.5 \cdot 10^2$	1.3
N $\text{MBr}_4 + \text{SCN}^-$	$\rightarrow \text{MBr}_3\text{SCN} + \text{Br}^-$	(8.7±0.4)·10 ⁴ (V)	$2.2 \cdot 10^4$	—	—	—
O $\text{MBr}_3\text{SCN} + \text{Br}^-$	$\rightarrow \text{MBr}_4 + \text{SCN}^-$	14±1 (V)	—	—	—	—
P $t\text{-MBr}_2(\text{SCN})_2 + \text{SCN}^-$	$\rightarrow \text{MBr}(\text{SCN})_3 + \text{Br}^-$	(1.2±0.2)·10 ⁴ (V)	$6.0 \cdot 10^3$	—	—	—

Acid Hydrolysis

	$10k_{\text{Au}}/\text{s}^{-1}$	$10^2 (k_{\text{Au}}/m) \text{s}^{-1}$	$10^5 k_{\text{Pt}}/\text{s}^{-1}$	$10^5 (k_{\text{Pt}}/m) \text{s}^{-1}$	$10^{-3} k_{\text{Au}}/k_{\text{Pt}}$
Q $\text{MCl}_4 + \text{H}_2\text{O}$	0.22^a	0.55	4.0 ± 0.2 (I)	1.0	0.6
R $\text{MCl}_3\text{Br} + \text{H}_2\text{O}$	—	—	7.9 ± 0.4 (I)	7.9	—
S $\text{t-MCl}_2\text{Br}_2 + \text{H}_2\text{O}$	—	—	0.90 ± 0.4 (I)	0.45	—
T $\text{c-MCl}_2\text{Br}_2 + \text{H}_2\text{O}$	—	—	13.0 ± 1.0 (I)	6.5	—
U $\text{MClBr}_3 + \text{H}_2\text{O}$	—	—	4.6 ± 0.3 (I)	4.6	—
V $\text{c-MCl}_2\text{Br}_2 + \text{H}_2\text{O}$	—	—	2.2 ± 0.2 (I)	1.1	—
W $\text{MCl}_3\text{Br} + \text{H}_2\text{O}$	—	—	1.05 ± 0.08 (I)	1.05	—
X $\text{MBr}_4 + \text{H}_2\text{O}$	2.45^b	6.13	19 ± 2 (I)	4.8	1.2

Halide Anations

	$10^{-4} k_{\text{Au}}/\text{M}^{-1} \text{s}^{-1}$	$10^{-4} (k_{\text{Au}}/m) \text{N}^{-1} \text{s}^{-1}$	$10^2 k_{\text{Pt}}/\text{M}^{-1} \text{s}^{-1}$	$10^2 (k_{\text{Pt}}/m)/\text{M}^{-1} \text{s}^{-1}$	$10^{-5} k_{\text{Au}}/k_{\text{Pt}}$
Y $\text{MCl}_3\text{H}_2\text{O} + \text{Cl}^-$	0.235^c	0.235	0.52 ± 0.02 (I)	0.52	4.5
Z $\text{MCl}_3\text{H}_2\text{O} + \text{Br}^-$	—	—	1.3 ± 0.7 (I)	1.3	—
A $\text{c-MCl}_2\text{BrH}_2\text{O} + \text{Br}^-$	—	—	1.45 ± 0.11 (I)	1.45	—
Ä $\text{MBr}_3\text{H}_2\text{O} + \text{Cl}^-$	—	—	3.0 ± 1.0 (I)	3.0	—
Ö $\text{MBr}_3\text{H}_2\text{O} + \text{Br}^-$	7.6^b	7.6	12.5 ± 1.0 (I)	12.5	6.1

Values from a) Ref. 42 b) Ref. 5 c) Ref. 6

Table II. Rate constants at 25.0°C for 1.00 M perchlorate medium; $\bigcirc$ denotes the leaving ligand.

Reac- tion No.	Sub- strate ligand complex	$k/M^{-1}s^{-1}$						$k/mQ^2/M^{-1}s^{-1}$						
		H ₂ O	Cl ⁻	Br ⁻	DMSO	C ₂ H ₄	SCN ⁻	I ⁻	Cl ⁻	Br ⁻	DMSO	C ₂ H ₄	SCN ⁻	I ⁻
(1)		7.3·10 ⁻⁷ a	-	(4.8±0.6)·10 ⁻⁵	(3.2±0.2)·10 ⁻³	(11±0.1)·10 ⁻³	(1.00±0.05)·10 ⁻²	(1.96±0.16)·10 ⁻²	-	3.0·10 ⁻⁴	9.0·10 ⁻⁵	2.8·10 ⁻⁴	6.3·10 ⁻²	0.12
(2)		-	(5.2±0.2)·10 ⁻³	(2.07±0.1)·10 ⁻²	(2.79±0.10)·10 ⁻²	(9.1±0.8)·10 ⁻³	0.10±0.01	0.38±0.02	2.6·10 ⁻²	0.10	9.3·10 ⁻³	9.1·10 ⁻³	0.5	1.9
(3a)		-	-	-	-	(4.0±0.4)·10 ⁻³	-	-	-	-	-	2.0·10 ⁻³	-	-
(3b)		1.8·10 ⁻⁶ b	-	(6.7±0.2)·10 ⁻³	(1.42±0.15)·10 ⁻³	(5.9±0.4)·10 ⁻³	0.30±0.02	0.31±0.03	-	3.4·10 ⁻³	70·10 ⁻⁴	3.0·10 ⁻³	0.15	0.16
(4)		-	(8.3±0.3)·10 ⁻²	0.35±0.05	(2.53±0.15)·10 ⁻²	(3.6±0.5)·10 ⁻²	3.15±0.20	7.3±0.5	4.2·10 ⁻²	0.18	1.3·10 ⁻²	1.8·10 ⁻²	1.6	3.7
(5)		-	0.46±0.03 c	1.7±0.2	(1.2±0.1)·10 ⁻²	(3.5±0.3)·10 ⁻²	16.0±0.9	39±2	9.2·10 ⁻²	0.34	3.6·10 ⁻²	3.5·10 ⁻²	3.2	7.8
(6)		-	(2.66±0.04)·10 ⁻² c	0.21±0.003 c	(8.4±0.5)·10 ⁻⁵	(1.0±0.1)·10 ⁻²	1.33±0.02 c	9.4±0.2 c	2.7·10 ⁻⁴	2.1·10 ⁻³	1.9·10 ⁻⁴	2.5·10 ⁻³	1.3·10 ⁻²	9.4·10 ⁻²

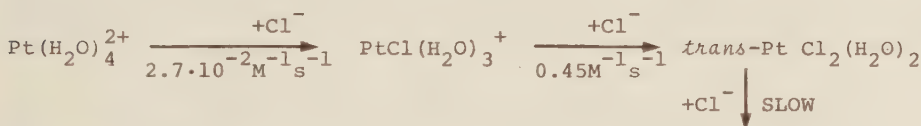
Values from a) Ref. 37, b) Ref. 78, c) Ref. 39. a) and b) transformed to second-order rate constants.

of *trans*-PtCl₂(H₂O)₂. (II)

Solutions of *cis*-dichlorodiaquaplatinum(II), *cis*-PtCl₂(H₂O)₂, were obtained by aging aqueous solutions of K₂PtCl₄ with sodium hydroxide for about 20 h at 25°C. After this time, the platinum is mainly in the form *cis*-PtCl₂(OH)₂²⁻.^{62,63} By addition of perchloric acid the complex *cis*-PtCl₂(H₂O)₂ is formed immediately. Solutions of *cis*-PtBr₂(H₂O)₂ were prepared correspondingly from K₂PtBr₄. (I,II).

Solutions of *trans*-PtCl₂(H₂O)₂ were prepared by aging Pt(H₂O)₄²⁺ solutions with excess sodium chloride (II). The following reactions take place (see ref. 39).

(7)



Since the subsequent chloride anation of *trans*-PtCl₂(H₂O)₂ is very slow the complex *trans*-PtCl₂(H₂O)₂ will accumulate in the solution.

3.2. Kinetics

The kinetics of the platinum(II) systems have been investigated by conventional spectrophotometry and those of gold(III) by stopped-flow techniques. The experiments were always arranged to give pseudo first-order reactions.

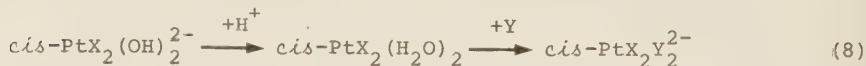
Attempts were made to perform the experiments in such a way that the rates of reaction could be described by as few parameters as possible. If feasible, the substrate complexes were prepared separately as e.g. in the investigation of the solvent path (II and III) where the six complexes PtCl_n(H₂O)_{4-n}²⁻ⁿ, n = 0,1,2,3,4, including *cis*- and *trans* isomers for n=2, were prepared and their kinetics with entering ligands were studied.

In other cases equilibrated solutions containing mainly two or three complexes were used as starting solutions in the kinetics, for example in the study of the mixed chloro-bromo complexes of

platinum(II) and gold(III) (e.g. reactions (4), (5) and (8) in IV). Different distributions of the metal between the species $MCl_{4-n}Br_n^{j-}$; $n = 0, 1, 2, 3, 4$ were obtained by variation of the quotient $[Br^-]/[Cl^-]$.

In the study of the substitution of halide by thiocyanate in AuX_4^- , $X=Cl, Br, (V)$ it was not feasible to use this technique because of the rapid succeeding reduction of the gold(III)-chloro-bromo-thiocyanato complexes to gold(I) by thiocyanate.

In some cases, it was possible to start from hydroxo-complexes. For example, in the study of reaction (2) and (3) in I, the starting complexes $cis-PtCl_2(OH)_2^{2-}$ and $cis-PtBr_2(OH)_2^{2-}$ were first prepared. By addition of a mixture of HBr and $HClO_4$ or HCl and $HClO_4$, the desired substrate complexes are rapidly formed:



Where $X=Cl, Br$; $Y=Br, Cl$.

Other examples are reactions (7) in IV and (2) in V, where the starting complexes were $AuCl_3OH^-$ and $AuBr_3OH^-$, respectively.

Except in a few cases, large excess of entering ligand was used to suppress reverse reactions, and consequently it was not possible to avoid subsequent processes. These were, however, eliminated by extrapolation, and the wavelengths were chosen to minimize their influence as much as possible. For example, in the study of reactions (1), (2) and (3) in paper I the absorbance change due to subsequent reactions was eliminated by using isosbestic wavelengths for the complexes formed in those processes. A valuable help in planning the experiments was, therefore, the spectra of equilibrated solutions and of individual complexes calculated from spectra of equilibrated solutions and equilibrium constants. (Figures 1 and 2 in I, Figure 2 and 3 in IV and Figure 2 in V).

Table III. Stepwise Equilibrium Constants K_n , defined by

$$K_n = \frac{k_{nBr}}{k_{nCl}} = \frac{[MCl_{3-n}Br_{n+1}^{j-}][Cl^-]}{[MCl_{4-n}Br_n^{j-}][Br^-]}, \quad M = Au, Pt; j = 1, 2, \text{ and } K_0^{SCN} = \frac{[AuBr_3SCN^-][Br^-]}{[AuBr_4^-][SCN^-]}$$

Reaction	K_n		$M = Au$		$M = Pt$	
		(kinetics) (Ref 44)		(spectro- photometric)		(kinetics)
$MCl_4^{j-} + Br^- \rightleftharpoons MCl_3Br^{j-} + Cl^-$	K_0	243 $\pm$ 40	288	10.0 $\pm$ 0.2	11.7 $\pm$ 1.0	
$MCl_3Br^{j-} + Br^- \rightleftharpoons MCl_2Br_2^{j-} + Cl^-$	K_1	98 $\pm$ 20	135	6.3 $\pm$ 0.2	-	
$MCl_3Br^{j-} + Br^- \rightleftharpoons cis-MCl_2Br_2^{j-} + Cl^-$	K_{1c}	64 $\pm$ 13 ^a	90 ^a	4.2 $\pm$ 0.2 ^a	-	
$MCl_3Br^{j-} + Br^- \rightleftharpoons trans-MCl_2Br_2^{j-} + Cl^-$	K_{1t}	34 $\pm$ 7 ^a	45	2.1 $\pm$ 0.1 ^a	-	
$MCl_2Br_2^{j-} + Br^- \rightleftharpoons MClBr_3^{j-} + Cl^-$	K_2	49 $\pm$ 10	64.6	1.8 $\pm$ 0.1	-	
$cis-MCl_2Br_2^{j-} + Br^- \rightleftharpoons cis-MClBr_3^{j-} + Cl^-$	K_{2c}	73 $\pm$ 15 ^a	97 ^a	2.7 $\pm$ 0.1 ^a	-	
$trans-MCl_2Br_2^{j-} + Br^- \rightleftharpoons trans-MClBr_3^{j-} + Cl^-$	K_{2t}	153 $\pm$ 30 ^a	194	5.4 $\pm$ 0.2 ^a	-	
$MClBr_3^{j-} + Br^- \rightleftharpoons MBr_4^{j-} + Cl^-$	K_3	17 $\pm$ 5	23.4	0.63 $\pm$ 0.06	1.0 $\pm$ 0.1	
$AuBr_4^- + SCN^- \rightleftharpoons AuBr_3SCN^- + Br^-$	K_0^{SCN}	(6.2 $\pm$ 0.7) $\cdot 10^3$				

a) Calculated, assuming a statistical distribution $[cis]/[trans] = 2:1$

3.3. Equilibria

The stepwise equilibrium constants for the mixed chloro-bromo complexes of Pt(II) and Au(III) are given in Table III. For the platinum(II) system, the constants were calculated from spectrophotometric equilibrium measurements using the UNIVAC 1108 computer in Lund and the least-squares minimizing program SPEFO.⁶⁴ The constants K_0 and K_3 were also calculated from the rate constants of forward and reverse reactions.(I).

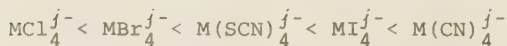
For the gold(III) system the equilibrium constants were obtained exclusively from rate constants of forward and reverse reactions.

The mixed chloro- and bromo-thiocyanato complexes of gold(III) are thermodynamically unstable (V). A rapid reduction within less than one second to gold(I) complexes takes place. In spite of this, it was possible to evaluate the first stepwise equilibrium constant in the bromo-thiocyanato system from the rate constants for the rapid ligand substitution process preceeding the reduction(V).

4. STABILITIES

It is obvious from Table III that there is an excellent agreement between the equilibrium constants determined from rate constants of forward and reverse reactions and those based on spectrophotometric equilibrium measurements, both in the case of gold and platinum.

The stabilities of gold(III) and platinum(II) halide and pseudo-halide complexes vary in the order ($j=1,2$)



as estimated from calculations of β_4 from the systems.^{65,66} However, the difference in stability between the gold(III) complexes in this series is much larger than that of the corresponding platinum(II) complexes. This is confirmed by the present results (I,IV) in Table III. The relative stability defined by

$$\beta_{4\text{Br}}/\beta_{4\text{Cl}} = K_0 \cdot K_1 \cdot K_2 \cdot K_3 \quad (9)$$

is $2.0 \cdot 10^7$ for the gold(III) complexes and only 133 in the platinum(II) system.

For both the platinum(II) and the gold(III) systems, all the complexes, including the *cis* and *trans*-isomers, are present at equilibrium in about their statistically expected relative amounts (I,IV), which is also a reasonable result for mixed complexes containing two ligands with similar properties. The thiocyanato complexes of Au(III) studied in V, are much more stable than the bromo and the chloro complexes.⁶⁵ The reported overall stability constants, β_4 , are about 10^{45} (SCN^-), 10^{34} (Br^-) and 10^{26} (Cl^-).

5. LIGAND SUBSTITUTION REACTIONS

For a given substrate, the k_1 -term in the simple rate law (2) is independent of the nature of the entering ligand Y. Figure 3 shows two possible intimate mechanisms for square-planar substitutions, which can explain this behaviour. In Figure 3a, the mechanism for the k_1 -term is dissociative, in Fig. 3b, the rate-determining step is an associative reaction with the solvent.

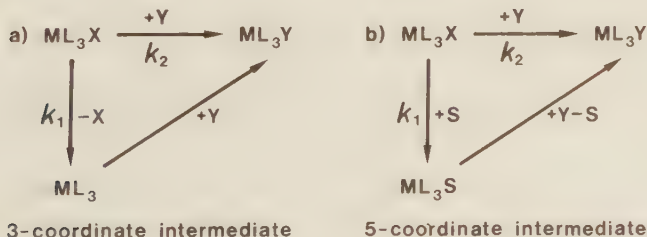


Figure 3. Ligand substitutions in square planar complexes. The k_1 -path corresponds either to (a) a dissociative mechanism or to (b) an associative mechanism.

With steady-state conditions for the intermediate aqua complex the pseudo first-order rate constant is described by eqn. (15) (compare eqn. (2) in III)

$$k_{\text{exp}} = k'_{-n\text{Cl}} \times \frac{1 + \frac{k_{n\text{Cl}}[\text{Cl}^-]}{k_{n\text{Br}}[\text{Br}^-]}}{1 + \frac{k'_{-n\text{Cl}}}{k'_{-(n+1)\text{Br}}} \times \frac{k_{n\text{Cl}}[\text{Cl}^-]}{k_{n\text{Br}}[\text{Br}^-]}} + k_{n\text{Cl}}[\text{Cl}^-] + k_{n\text{Br}}[\text{Br}^-] \quad (15)$$

where the first term corresponds to the k_1 -term in the simple eqn. (2).

For the concentrations of entering halide used in I (M=Pt) the reactions (12) and (13) proceed entirely *via* the reversible acid hydrolysis reactions in scheme (14). The experimental rate constants are then given by (16) for reaction (12) and by (17) for reaction (13), corresponding to the first term in (15). (See also eqn. (6)):

$$k_{\text{exp}} = \frac{k'_{0\text{Cl}} K'_{-1\text{Br}} [\text{Br}^-]}{k'_{-0\text{Cl}} [\text{Cl}^-] + k'_{-1\text{Br}} [\text{Br}^-]} \left(1 + \frac{([\text{Cl}^-]/[\text{Br}^-]) K'_{1\text{Br}}}{K'_{0\text{Cl}}} \right) \quad (16)$$

$$k_{\text{exp}} = \frac{k'_{4\text{Br}} K'_{-3\text{Cl}} [\text{Cl}^-]}{k'_{-4\text{Br}} [\text{Br}^-] + k'_{-3\text{Cl}} [\text{Cl}^-]} \left(1 + \frac{([\text{Br}^-]/[\text{Cl}^-]) K'_{3\text{Cl}}}{K'_{4\text{Br}}} \right) \quad (17)$$

$K'_{n\text{Cl}} = k'_{n\text{X}}/k'_{-n\text{X}}$, $n=0,1$ for $\text{X}=\text{Cl}$ and $n=3,4$ for $\text{X}=\text{Br}$, denote acid hydrolysis equilibrium constants. These equations can be further simplified in paper I, since the experimental conditions were chosen such that $k'_{-0\text{Cl}} [\text{Cl}^-] \gg k'_{-1\text{Br}} [\text{Br}^-]$ and $k'_{-4\text{Br}} [\text{Br}^-] \gg k'_{-3\text{Cl}} [\text{Cl}^-]$ so we arrive at

$$k_{\text{exp}} = k'_{1\text{Br}} + K'_{0\text{Cl}} k'_{-1\text{Br}} \times \frac{[\text{Br}^-]}{[\text{Cl}^-]} \quad (18)$$

$$k_{\text{exp}} = k'_{3\text{Cl}} + K'_{4\text{Br}} k'_{-3\text{Cl}} \times \frac{[\text{Cl}^-]}{[\text{Br}^-]} \quad (19)$$

For the reactions (12) and (13) in the gold(III) system (IV) the k_1 -term is too small to be observed. In that case eqn. (15) is reduced to

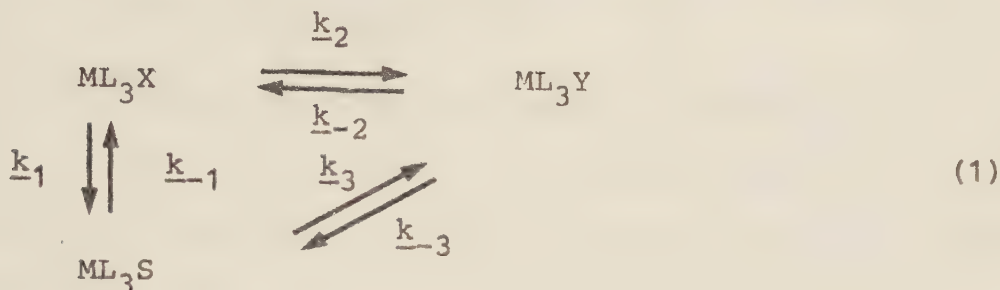
Solvent Paths for Square-Planar Substitutions. Part 2.* Reactions between Aqua Chloroplatinates(II) and Ethene

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The kinetics for the reactions between the complexes $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$, $n=0,1,2,3,4$ (including cis- and trans-isomers for $n=2$) and ethene have been studied. In the case of trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$, product analysis shows that both the chloride ligand and the aqua ligand are substituted by ethene in two parallel paths, differing in rate by a factor of only 1.5. The experiments show that ethene, and probably olefins in general, are inefficient entering ligands, similar to dimethyl sulphoxide. Steric reasons might be responsible. Changes in relative cis- and trans-effects are compatible with an associative mechanism. The aqua complexes are sufficiently reactive with ethene to be steady-state intermediates in associative solvent paths. Reaction models and rate laws for associative square-planar substitutions are discussed, with special reference to reported non-reactivity of solvento intermediates in some previously studied systems.



Aqua complexes appear as intermediates in square-planar substitution reactions in aqueous solution, if an associative mechanism for the solvent path is operative. In general terms, the mechanism can be written as scheme (1), S=solvent:

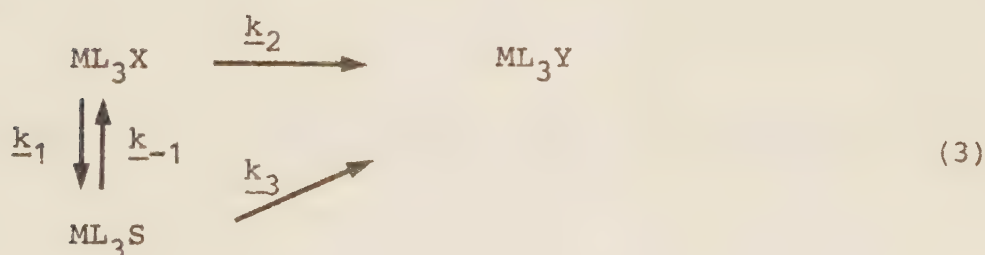


For excess X and Y compared to substrate complex this mechanism gives the pseudo first-order rate constant (2)

$$k_{\text{exp}} = \frac{k_1 + \frac{k_1 k_{-2} [X]}{k_2 [Y]}}{1 + \frac{k_{-1} [X]}{k_3 [Y]}} + k_{-2} [X] + k_2 [Y] \quad (2)$$

if the solvento intermediate ML_3S is assumed to be present in steady-state concentrations and if the

condition $(k_2/k_{-2}) = (k_1/k_{-1})(k_3/k_{-3})$ is used. If the reverse reactions described by k_{-2} and k_{-3} are negligible, scheme (1) simplifies to (3),



with the rate constant (4), in which the first term describes the contribution from the solvent path via ML_3S .

$$k_{\text{exp}} = \frac{k_1}{1 + \frac{k_{-1} [X]}{k_3 [Y]}} + k_2 [Y] \quad (4)$$

The special case of a rapid equilibrium between the parent complex ML_3X and the solvento intermediate ML_3S for excess X gives the rate constant (5)

$$\underline{k}_{\text{exp}} = \frac{\underline{k}_2 + \underline{k}_3 \underline{K}/[X]}{1 + \underline{K}/[X]} \times [R] \quad (5)$$

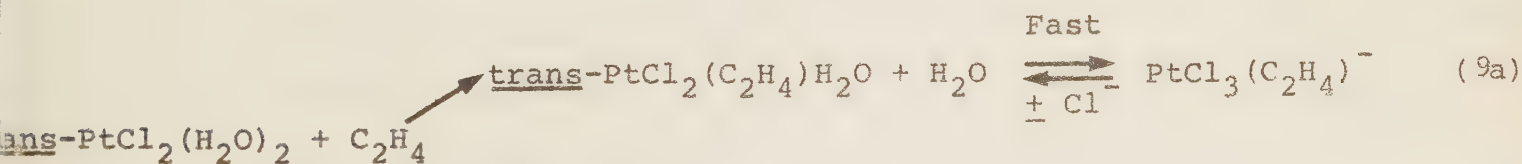
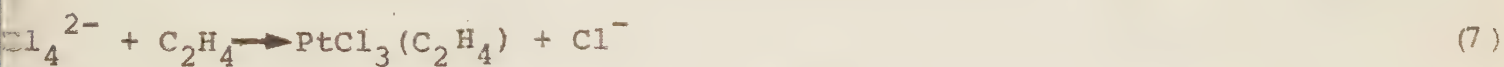
where $\underline{K} = \underline{k}_1/\underline{k}_{-1}$ and R is the excess reactant (Y or complex).

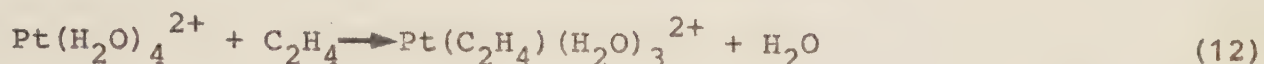
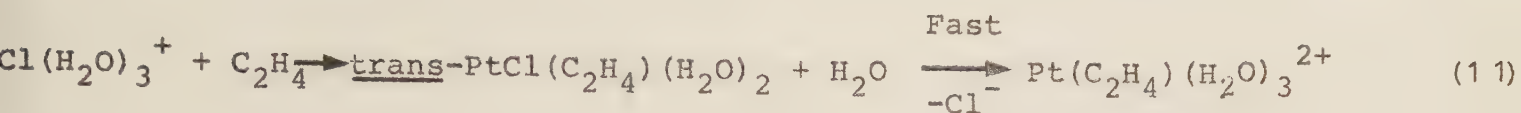
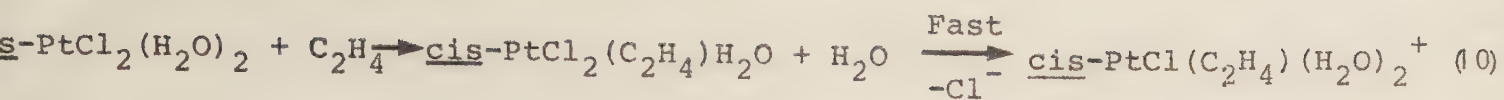
When no extra leaving ligand is added in the experiments i.e. $\underline{k}_{-1}[X] \ll \underline{k}_3[Y]$, eqn. (4) is reduced to the well-known expression (6).

$$\underline{k}_{\text{exp}} = \underline{k}_1 + \underline{k}_2[Y] \quad (6)$$

A necessary condition for rate laws (2), (4) and (6) is that the solvento intermediates are sufficiently reactive to satisfy the steady-state approximation. Information on their reactivities is therefore relevant in this context.

We have recently reported kinetic data for the reactions between the complexes $PtCl_n(H_2O)_{4-n}^{2-n-}$; $n=0,1,2,3,4$ and the nucleophiles $Y=Cl^-$, Br^- , I^- , SCN^- and DMSO.¹ The experiments supported scheme (3) and gave rate constants of the forms (4) and (6). We will here report supplementary data for ethene as entering ligand in these complexes. We have studied reactions (7) to (12):





We have found only two quantitative kinetic studies of olefins as entering ligands for square-planar complexes in the literature.^{2,3} The conclusions in these papers are discordant. Milburn and Venanzi,² in their study of some PtCl_4^{2-} -olefin reactions, explained the absence of an observable solvent path in terms of a lower reactivity between the olefin and $\text{PtCl}_3\text{H}_2\text{O}^-$ compared to PtCl_4^{2-} , whereas Green and Wilson³ found that $\text{PtCl}_3\text{H}_2\text{O}^-$ reacts readily with ethene. Other cases of non-reactivity of aqua species have also been suggested⁴ (vide infra).

EXPERIMENTAL

Chemicals and Solutions. - Potassium tetrachloroplatinate(II) from Johnson and Matthey was used directly. Solutions (1 to 13 mM) of the complexes $\text{Pt}(\text{H}_2\text{O})_4^{2+}$, $\text{PtCl}(\text{H}_2\text{O})_3^+$, cis- and trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$ in 1.00 M perchloric acid were prepared as described previously.¹ Zeise's salt, $\text{KPtCl}_3(\text{C}_2\text{H}_4)$, was prepared according to Chatt and Searle.⁵ The ethene was C.P. grade from Matheson Gas Products. Ethene stock solutions (ca. 5 mM) were prepared by saturation of aqueous perchloric acid (1.00 M) or perchloric/hydrochloric acid (1.00 M) with gas for 3 h at 25 °C and atmospheric pressure using the apparatus described in Ref. 5. The solutions were analyzed for ethene by addition of excess bromine and subsequent determination of the residual free bromine by

addition of iodide and spectrophotometric analysis for I_3^- at 353 nm; $\epsilon_{I_3^-} = 26400 \text{ cm}^{-1} \text{ M}^{-1}$.

Kinetics. - In the experiments with excess ethene, the kinetics for reactions (7), (9), (10), (11) and (12) were started by rapidly mixing 1 ml of platinum complex solution with 100 ml of ethene-chloride or ethene solution at 25.00°C . For reaction (8), 10 ml of a pre-equilibrated platinum complex solution ($C_{Pt} = 0.10 \text{ mM}$, $C_{Cl} = 0.020 \text{ M}$, giving 61% $PtCl_4^{2-}$ and 39% $PtCl_3H_2O^-$ at equilibrium, cf. Ref. 9) was mixed with 90 ml of an ethene-chloride solution.

In the experiments on reaction (7) with excess complex, 10 ml of ethene stock solution and 90 ml of $PtCl_4^{2-}$ solution were mixed. A sample of the reacting solution was transferred to a cell in the thermostated holder of a Zeiss PMQ II Spectrophotometer, kept at $(25.00 \pm 0.02)^\circ\text{C}$, whereupon the cell was stoppered. The ionic strength and hydrogen ion concentration were 1.00 M , supported by perchloric acid. Excess chloride was added to the ethene solutions as hydrochloric acid in the experiments with $PtCl_4^{2-}$ and trans- $PtCl_2(H_2O)_2$. Excess ethene or complex gave pseudo first-order kinetics. Reverse reactions were negligible because of the high stability of the ethene complexes formed. For the low concentrations of ethene used (0.5 to 5 mM) there was no indication of formation of complexes containing more than one ethene ligand. Rate constants were calculated directly from the absorbance vs. time plots using a least-squares programme. Table 1 reviews the experiments.

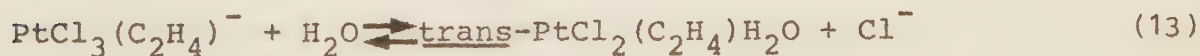
Side reactions. - Ethene-chloro-aqua complexes decompose slowly in aqueous solution, the ethene probably being oxidized to acetaldehyde.⁶ These processes are slow and kinetically well

separated from the ligand substitution reactions studied here. The least stable complex appears to be cis-PtCl(C₂H₄)(H₂O)₂⁺, formed in reaction (10), whereas the platinum-ethene-aqua complex Pt(C₂H₄)(H₂O)₃²⁺ is stable in aqueous perchloric acid solution for several months.

Spectra. - The absorption spectra given in Figure 1 were recorded at 25.0 °C using a Beckman Model 25 recording spectrophotometer. The spectrum of PtCl₃(C₂H₄)⁻ was recorded using a solution with $\underline{C}_{\text{Pt}} = 0.1 \text{ mM}$ and $\underline{C}_{\text{Cl}} = 0.050 \text{ M}$ or 1.00 M and that of trans-PtCl₂(C₂H₄)(H₂O) using a 0.1 mM solution of Zeise's salt in 1.00 M perchloric acid. No extra chloride was added. The latter solution contains more than 97 % of the platinum as trans-PtCl₂(C₂H₄)H₂O, cf. reaction (13).

CALCULATIONS AND RESULTS

Reaction Products. - The chloride ligands trans to the olefin are labile due to the large trans-effect of ethene. The following rapid aquation equilibria must be considered in the product analysis:



The acid hydrolysis equilibrium constants are $\underline{K}_{(13)} = 3 \times 10^{-3} \text{ M}$, $\underline{K}_{(14)} \sim 1 \times 10^{-4} \text{ M}$, and $\underline{K}_{(15)} \sim 1 \times 10^{-3} \text{ M}$. $\underline{K}_{(13)}$ has been measured by Leden and Chatt,⁷ whereas the values for $\underline{K}_{(14)}$ and $\underline{K}_{(15)}$ can be estimated from an analogy with the constants for the corresponding Pt(II)-DMSO-Cl⁻-H₂O complexes.⁸ Thus, for the experimental concentrations of chloride given in Table 1, PtCl₃(C₂H₄)⁻

will be the sole reaction product in reaction (7), trans- $\text{PtCl}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_2^+$ in reaction (9b), cis- $\text{PtCl}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_2^+$ in reaction (10) and $\text{Pt}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_3^{2+}$ in reactions (11) and (12). Reactions (8) and (9a) will give equilibrium mixtures of trans- $\text{PtCl}_2(\text{C}_2\text{H}_4)\text{H}_2\text{O}$ and $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ as the reaction products, except for the highest concentration of chloride used in reaction (9a) (50 mM), where more than 95% of the platinum will be present as Zeise's anion.

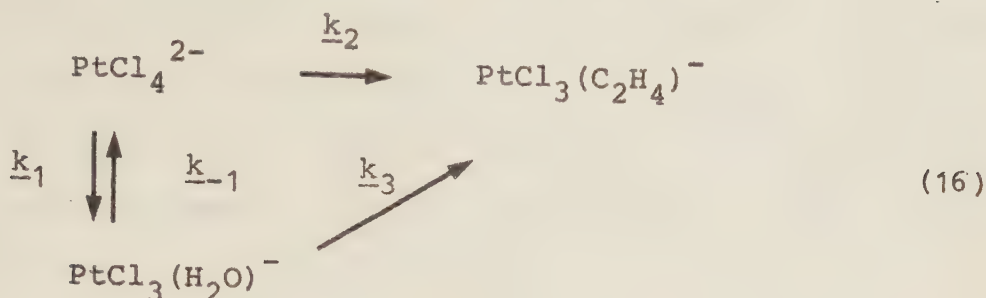
The reaction product for reaction (7) was identified by a comparison of the spectrum for the equilibrated solution with the independently recorded spectrum for $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ in Figure 1.

Absorption spectra for the reaction products of reactions (10) - cis- $\text{PtCl}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_2^+$ - and (11) and (12) with and without addition of excess chloride - trans- $\text{PtCl}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_2^+$ and $\text{Pt}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_3^{2+}$ - are also included in the Figure. The dashed line in Figure 1 represents the spectrum of the equilibrated solution formed in reaction (9) for $[\text{Cl}^-]=50$ mM. This spectrum is a superposition of the spectra for trans- $\text{PtCl}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_2^+$ and $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ in the ratio $(1.5 \pm 0.2):1$ which directly gives the ratio between the two over-all rate constants for the parallel paths (9b) and (9a) (vide infra).

Kinetics. - Reactions (10), (11) and (12) are simple substitutions of aqua ligands by ethene. Figure 2 shows plots of the observed rate constants vs. the concentration of excess ethene and Table 2 gives the rate constants obtained from the slopes of these plots.

Reaction (7) was studied using excess of chloride and PtCl_4^{2-} or ethene. Reaction (8) was studied using excess of chloride and ethene and a pre-equilibrated solution of PtCl_4^{2-} .

(ca. 61%) and $\text{PtCl}_3(\text{H}_2\text{O})^-$ (ca. 39%), cf. Table 1. Scheme (3) takes the form (16) for these reactions.



For reaction (7), the observed rate constant for excess ethene is described by eqn. (4) where the ratio $[\text{X}]/[\text{Y}] = [\text{Cl}^-]/[\text{C}_2\text{H}_4] = 100$ was kept constant in all experiments, cf. Table 1. Figure 3a shows a plot according to eqn. (4). Introducing $k_{-1} = (5.2 \pm 0.2) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ from Ref. 9 and $k_3 = (9.1 \pm 0.8) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ from Table 2, the intercept of Figure 3a $(0.80 \pm 0.11) \times 10^{-6} \text{ s}^{-1}$ gives $k_1 = (4.7 \pm 0.5) \times 10^{-5} \text{ s}^{-1}$, in good agreement with previously determined values⁹ for the acid hydrolysis rate constant of PtCl_4^{2-} , $(4.0 \pm 0.2) \times 10^{-5} \text{ s}^{-1}$. The slope of the plot in Figure 3a gives $k_2 = (1.1 \pm 0.1) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$.

For excess tetrachloroplatinate(II) compared to ethene, all experiments on reaction (7) were performed using a constant, large excess of leaving ligand ($[\text{Cl}^-] = 0.900 \text{ M}$), which determines the distribution of platinum between PtCl_4^{2-} and $\text{PtCl}_3(\text{H}_2\text{O})^-$ in rapid equilibrium with each other, cf. scheme (16). The equilibrium mixture of PtCl_4^{2-} and $\text{PtCl}_3\text{H}_2\text{O}^-$ reacts via the two parallel, slow paths denoted by k_2 and k_3 to the common product $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$. The observed pseudo first-order rate constant is described by eqn. (5) where $[\text{R}] = \underline{C}_{\text{Pt}}$ denotes the total concentration of platinum and $\underline{K}$ is the equilibrium constant⁹ $k_1/k_{-1} = 7.7 \times 10^{-3} \text{ M}$. For the high concentration of leaving ligand used, the term $\underline{K}/[\text{X}] \ll 1$ and eqn. (5) can be

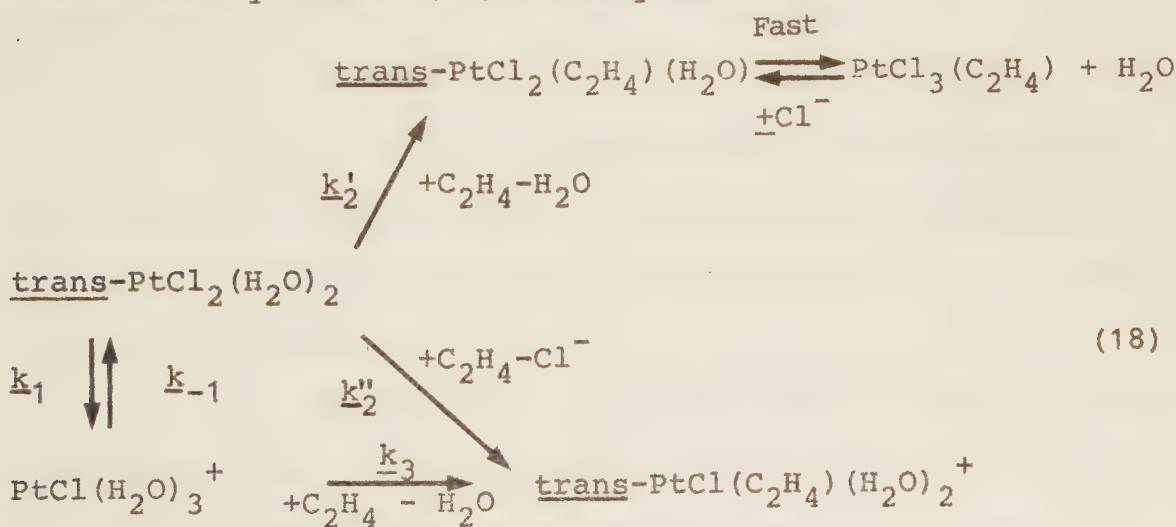
simplified to (17). Figure 3b

$$\underline{k}_{\text{exp}} = (\underline{k}_2 + \underline{k}_3 K[\text{Cl}^-]^{-1}) \underline{C}_{\text{Pt}} \quad (17)$$

shows a plot according to eqn. (17). The slope $(1.17 \pm 0.03) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and the value of $\underline{k}_3 K[\text{Cl}^-]^{-1} = (7.8 \pm 2.0) \times 10^{-5} \text{ M}^{-1} \text{ s}^{-1}$ (using the $\underline{k}_3$ value in Table 2) give $\underline{k}_2 = (1.09 \pm 0.05) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, in good agreement with the determination in Fig. 3a from the experiments with excess ethene.

For reaction (8), the aqua intermediate $\text{PtCl}_3(\text{H}_2\text{O})^-$ and the parent complex, PtCl_4^{2-} can also be considered to be in rapid equilibrium with each other, and the observed first-order rate constant is described by eqn. (5) with $\text{R}=\text{C}_2\text{H}_4$. Figure 3c shows a plot according to eqn. (5). From the slope, $(3.3 \pm 0.1) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and the values⁹ of $\underline{K}=7.7 \times 10^{-3} \text{ M}$ and $\underline{k}_2=(1.1 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$ (Table 2), we obtain $\underline{k}_3=(9.1 \pm 0.8) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$.

Reaction (9) was also studied using excess chloride and ethene. The product analysis shows that the reaction between ethene and trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$ takes place via the two parallel paths denoted (9a) and (9b). Thus, reaction (9) can be described by scheme (18). Steady-state



conditions for the aqua intermediate $\text{PtCl}(\text{H}_2\text{O})_3^+$ give the observed pseudo first-order rate constant for excess ethene of eqn. (19). The ratio $[\text{Cl}^-]/[\text{C}_2\text{H}_4] = 10$ was constant in all

$$\underline{k}_{\text{exp}} = \frac{\underline{k}_1}{1 + \underline{k}_{-1}[\text{Cl}^-]/\underline{k}_3[\text{C}_2\text{H}_4]} + (\underline{k}_2' + \underline{k}_2'')[\text{C}_2\text{H}_4] \quad (19)$$

experiments, cf. Table 1. Figure 3d shows a plot according to eqn. (19). The first term in eqn. (19) corresponds to the small intercept, which is approximately $(1.0 \pm 0.2) \times 10^{-6} \text{ s}^{-1}$. Introducing the rate constants $\underline{k}_{-1} = 0.46 \text{ M}^{-1} \text{ s}^{-1}$ from Ref. 10 and $\underline{k}_3 = 3.5 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ from Table 1 we find that $\underline{k}_1$ is approximately $(1.3 \pm 0.3) \times 10^{-4} \text{ s}^{-1}$, in satisfactory agreement with the separately determined¹⁰ acid hydrolysis rate constant for trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$ ($1 \times 10^{-4} \text{ s}^{-1}$).

The product analysis gives $\underline{k}_2''/\underline{k}_2' = 1.5 \pm 0.2$, since the first term in eqn. (19) can be neglected compared to $\underline{k}_2'[\text{C}_2\text{H}_4]$. The slope of the plot in Figure 3d gives the sum of the rate constants, $\underline{k}_2' + \underline{k}_2'' = (9.9 \pm 0.7) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. Thus, we obtain the values $\underline{k}_2' = (4.0 \pm 0.4) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ and $\underline{k}_2'' = (5.9 \pm 0.5) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ given in Table 2.

DISCUSSION

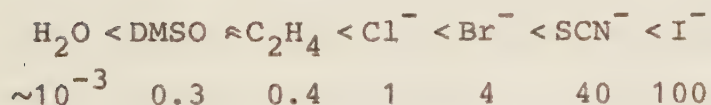
Table 2 gives a review of the rate constants. For comparison, corresponding values for dimethyl sulphoxide¹ have been included. We have also listed values of $\underline{k}/(\underline{n}\underline{O}^g)$ calculated as described previously.¹

Our rate constants for reactions (7) and (8) agree relatively well with those determined by Green and Wilson.³ G & W had to use complicated expressions to evaluate their constants from the rate of absorption of gaseous ethene by aqueous solutions of PtCl_4^{2-} , $\text{PtCl}_3\text{H}_2\text{O}^-$ and (probably cis-) $\text{PtCl}_2(\text{H}_2\text{O})_2$ in equilibrium with each other. A comparison with Milburn's and Venanzi's² previous data is given in Table 3.

The following conclusions can be drawn from the values in Tables 2 and 3:

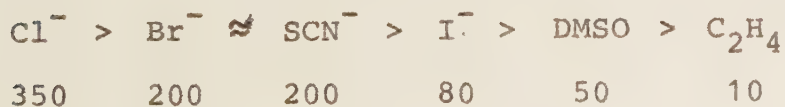
(i). Ethene behaves like an uncharged entering ligand, i.e. the ionic charge of the substrate complex has no influence on the rates ($Q=1.0\pm0.1$). M&V's data in Table 3 show similarly that alkylalcohol reacts with the same rate as ethene with PtCl_4^{2-} , whereas the rate increases slightly for the allylammonium ion and decreases for the allylsulphonate ion. The variations in rate with the substituents on the olefin are very small, which is reasonable, since the charged parts of the olefins are relatively far from the reaction centre.

(ii). Ethene, and probably olefins in general, cf. Table 3, are inefficient entering ligands, like dimethyl sulfoxide. We can put forward the following approximate sequence for entering-ligand-efficiency in these simple platinum(II)-chloro-aqua-complexes, water being the leaving group, cf. Ref. 1:



Specific steric requirements for the formation of the transition state might be responsible for the low efficiency of DMSO and ethene as nucleophiles.

(iii). We observed previously¹ that the relative trans-effect $\text{Cl}^-/\text{H}_2\text{O}$, which is 350 for chloride as entering ligand, varies with the nature of the entering nucleophiles. We can now include ethene in this series



and conclude that the relative trans-effect $\text{Cl}^-/\text{H}_2\text{O}$ decreases, when the trans-effect of the entering nucleophile increases. The relative cis-effect $\text{Cl}^-/\text{H}_2\text{O} = 0.5 \pm 0.2$, on the other hand, is independent of the nature of the entering nucleophile, including ethene. Both observations are in accord with a trigonal bipyramidal transition state, where there is a strong interaction between entering, leaving and trans-ligands, whereas the cis-ligands are much less involved. In agreement with this, the relative efficiency of leaving ligands also varies with the nature of the entering nucleophile, but this dependence is less regular.

Reaction Mechanisms. - The present results give further support to reaction scheme (3). Thus, the values of k_1 obtained by extrapolation of the plots in Figures 3a and 3d agree within the limits of error with the separately determined acid hydrolysis rate constants for PtCl_4^{2-} and trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$.

Table 4 compares the rate constants for the substitution of an aqua ligand in the complexes $\text{PtCl}_3\text{H}_2\text{O}^-$ and $\text{PtCl}(\text{H}_2\text{O})_3^+$ with those for the substitution of a chloride in the corresponding parent chloro complexes PtCl_4^{2-} and trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$ for various entering nucleophiles. The difference in reactivity between aqua complex and chloro complex is large (ca. 500) for entering ligands of low trans-effect like chloride and bromide, whereas the difference is much smaller (about 10) for nucleophiles high in the trans-effect series like iodide, thiocyanate, DMSO and ethene. In all cases studied, however, the aqua complexes are sufficiently reactive to function as steady-state intermediates in a solvent path according to schemes (3), (16) and (18).

One obvious reason for the non-appearance of one of the terms in the rate laws (2), (4) or (6) is the trivial fact that in some systems $k_1 \ll k_2[Y]$ and in others $k_1 \gg k_2[Y]$. For instance, the nature of the entering group is much more important for the reactions of gold(III) substrates than for those of palladium(II) or platinum(II). Therefore, the stepwise halide substitutions in the AuCl_4^- - Br^- -system¹¹ take place without any significant contribution by the solvent path in the bromide concentration range necessary for the experiments.* The reverse is true for the analogous PtCl_4^{2-} - Br^- -reactions,⁹ where the solvent path is predominant and it is necessary to increase the bromide concentration to very large values in order to observe the small contribution from the $k_2[Y]$ -term in eqn. (2).

The solvent path can also be quenched by the presence of large concentrations of leaving ligand, compare reaction schemes (1) and (3). The leaving group X and the entering group Y compete for the solvento intermediate. If the concentration of leaving ligand is increased, the first term in eqns. (2) and (4) will decrease and will sometimes become negligible compared to other terms in the rate equation.

* This does not imply, of course, that aqua complexes of Au(III) react slowly with nucleophiles. Compare, for instance, the rate constant¹² for the $\text{AuCl}_3\text{H}_2\text{O}$ - Cl^- -reaction ($2.3 \times 10^3 \text{ M}^{-1} \text{ s}^{-1}$) with that for the AuCl_4^- - Cl^- isotopic exchange¹³ ($1.5 \text{ M}^{-1} \text{ s}^{-1}$).

Milburn's and Venanzi's investigation,² performed using a large excess of leaving ligand, gives an example of such behaviour. M & V observed that the reaction path via $\text{PtCl}_3(\text{H}_2\text{O})^-$ was negligible, but their conclusion that the aqua complex is less reactive towards olefins than PtCl_4^{2-} is obviously not in agreement with our present results, nor with Green's and Wilson's observations.³

The discrepancy can be explained, if M&V's experimental design is considered. Using scheme (16) and their notations for the rate constants, we can estimate[†] $k_1 = k' = 4 \times 10^{-5} \text{ s}^{-1}$, $k_{-1} = k'' = 8 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $k_3 = k''' = 1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$. k_2 is given by M & V as $1.86 \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$. These values of the rate constants indicate that the first term in eqn. (4) will never amount to more than about 1% of the second term for the large concentrations of chloride used (1 M or 2 M). Thus, the experimental results of M & V can be explained by the general rate law (4), without any special assumptions about a non-reactivity of the solvento intermediate.

[†] The value of $k_3 = 1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ for the $\text{PtCl}_3\text{H}_2\text{O}^-$ -olefin reactions in general seems reasonable, since $\text{PtCl}_3\text{H}_2\text{O}^-$ reacts with ethene with a rate constant of $1.1 \times 10^{-2} \text{ M}^{-1} \text{ s}^{-1}$ (Table 2) and there is no significant difference in reactivity between the various olefins (Table 3). The acid hydrolysis rate constant k_1 is approximately independent of ionic strength⁹ whereas the chloride anation rate constant k_{-1} has been extrapolated to the ionic strength 2 M from values at 0.5 M and 1.0 M ionic strength.⁹

In this context it is interesting to examine other experimental studies,⁴ suggesting that solvento intermediates react slowly (or not at all) with the entering nucleophile, Y. For instance, Bekker and Robb¹⁴ have reported studies of the reactions between PdCl_4^{2-} and a series of substituted thioureas. Their experimental design was similar to that of M & V in that a large excess of leaving ligand was used. Linear plots through the origin of k_{exp} vs. $[Y]$ with slope k_2 were obtained for all values of $[Y]$ and $[X]$. To explain the absence of the solvent path in this particular case, the authors assumed that $k_3 \approx k_2$ using the notation in scheme (3). However, the steady-state conditions were fulfilled only for the highest concentrations of chloride used (2M), and in these experiments, the solvent path was effectively quenched, i.e. $k_1 k_3 / (k_3 [Y] + k_{-1} [X]) \ll k_2$, even if $k_3 \gg k_2$. For $[\text{Cl}^-] = 0.100 \text{ M}$ neither of the two conditions steady-state for $\text{PdCl}_3\text{H}_2\text{O}^-$ or a rapid equilibrium between PdCl_4^{2-} and $\text{PdCl}_3\text{H}_2\text{O}^-$ leading to eqn. (5) were fulfilled, so the rate expressions used were not applicable. Independent studies of the $\text{PdCl}_3\text{H}_2\text{O}^-$ -thiourea reaction have not been performed. Mureinik¹⁵ has suggested that thiocyanate is unreactive towards aqua complexes of platinum(II), viz. $\text{PtCl}_3\text{H}_2\text{O}^-$, but new experiments¹ have disproved this conclusion.

In cases where both terms of eqns. (2) and (4) contribute to the over-all reaction, a necessary condition for linear relationships of k_{exp} vs. $[Y]$ is obviously that the series of experiments are performed using constant ratios $[X]/[Y]$, both X and Y being present in excess compared to the substrate complex. Examples of such plots are given by the PtCl_4^{2-} -iodide- and DMSO-reactions,¹ the PtCl_4^{2-} -ethene and trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$ -ethene reactions in the present report and by the PtCl_4^{2-} -bromide and PtBr_4^{2-} -chloride reactions.⁹

If the condition $[X]/[Y]=\text{constant}$ is not fulfilled, curved plots of k_{exp} vs. $[X]$ and k_{exp} vs. $[Y]$ will be obtained, as has recently been pointed out by de Waal and Robb.¹⁶ This case is illustrated by Seguin's and Zador's study¹⁷ of the PtdienBr^+ -inosine reaction, which conforms to scheme (1) and where iteration methods were used for the evaluation of the rate constants.

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Figure Captions

FIGURE 1. Spectra of the complexes 1 - $\text{Pt}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_3^{2+}$, 2 - trans - $\text{PtCl}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_2^+$, 3 - trans- $\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{H}_2\text{O})$, 4 - $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ and 5-cis- $\text{PtCl}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_2^+$. The dashed spectrum was recorded using an equilibrated solution of reaction (9) with $C_{\text{Pt}}=1.09 \times 10^{-4}$ M, $[\text{C}_2\text{H}_4]=5.0$ mM, and $[\text{Cl}^-]=50$ mM. It is a superposition of spectra 2 and 4 in the ratio $(1.5 \pm 0.2):1$.

FIGURE 2. Observed rate constants for reactions (7)- $\bigcirc$; (10)- ∇ ; (11)- $\bigcirc$ and (12)- $\triangle$ vs. the concentration of excess ethene.

FIGURE 3. Observed rate constants for reactions (7),(8) and (9) vs. concentration of excess reactant, (a) - reaction (7) for excess ethene, (b) - reaction (7) for excess tetrachloroplatinate(II), (c) - reaction (8) for excess ethene and (d) - reaction (9) for excess ethene.

Rate constants for the reactions between $\text{PtCl}_{\underline{n}}(\text{H}_2\text{O})_{4-\underline{n}}^{2-\underline{n}}$, $\underline{n}=0,1,2,3,4$, and ethene at 25.0 °C and 1.00 M perchloric acid medium.

Reaction	$10^3 [\text{C}_2\text{H}_4]/\text{M}$	$10^3 [\text{Cl}^-]_{\text{added}}/\text{M}$	$10^4 \underline{C}_{\text{Pt}}/\text{M}$	λ/nm	$10^5 \underline{k}_{\text{exp}}/\text{s}^{-1}$
(7)	0.5	50	0.5	218	0.148 ± 0.020
	1.0	100	0.5	218	0.180 ± 0.020
	1.5	150	0.5	218	0.265 ± 0.020
	2.0	200	0.5	218	0.291 ± 0.025
	3.0	300	0.5	218	0.476 ± 0.035
	4.0	400	0.5	218	0.549 ± 0.020
	4.5	450	0.5	218	0.589 ± 0.020
	0.1	900	10.0	218	0.102 ± 0.015
	0.2	900	20.0	218	0.214 ± 0.020
	0.3	900	30.1	218	0.319 ± 0.025
	0.5	900	50.2	218	0.537 ± 0.025
	0.5	900	70.2	218	0.779 ± 0.039
	0.5	900	100.0	218	1.13 ± 0.05
(8)	1.0	20	1.0	287	0.34 ± 0.02
	2.0	20	1.0	287	0.66 ± 0.03
	3.0	20	1.0	287	0.97 ± 0.07
	4.0	20	1.0	287	1.31 ± 0.04
	4.4	20	1.0	287	1.45 ± 0.03
(9)	1.0	10	0.64	250	1.09 ± 0.12
	2.0	20	0.64	250	2.16 ± 0.15
	3.0	30	0.64	250	3.08 ± 0.16
	4.0	40	0.64	250	3.89 ± 0.18
	5.0	50	0.64	250	4.97 ± 0.11
(10)	1	-	0.2	250	3.6 ± 0.5
	3	-	0.2	250	10.7 ± 0.6
	5	-	0.2	250	18.1 ± 1.0
(11)	1.7	-	0.1	250	5.9 ± 0.3
	3.0	-	0.1	250	10.1 ± 0.7
	4.0	-	0.1	250	13.8 ± 1.0
	5.0	-	0.1	250	17.4 ± 1.0
(12)	0.98	-	1.32	220	0.94 ± 0.05
	2.0	-	1.0	220	2.03 ± 0.2
	2.45	-	1.32	220	2.6 ± 0.2
	3.0	-	1.0	220	3.0 ± 0.2
	3.92	-	1.32	220	3.9 ± 0.3
	4.0	-	1.0	220	4.0 ± 0.3
	4.90	-	1.32	220	5.0 ± 0.3
	5.0	-	1.0	220	5.0 ± 0.3

Second-order rate constants at 25.0 °C and a 1.00 M perchlorate medium for reactions of ethene with $\text{PtCl}_n(\text{H}_2\text{O})_{4-n}^{2-n}$, $n=0,1,2,3,4$. Rate constants for dimethyl sulphoxide from Ref. 1 have also been included. Values of $k/(nQ^{\frac{1}{2}})$ calculated as described in Ref. 1.

Reaction	Substrate complex	Leaving Ligand	$k/\text{M}^{-1} \text{ s}^{-1}$		$(k/nQ^{\frac{1}{2}})/\text{M}^{-1} \text{ s}^{-1}$	
			C_2H_4	DMSO [†]	C_2H_4	DMSO [†]
(7)	PtCl_4^{2-}	Cl^-	$(1.1 \pm 0.1) \times 10^{-3} \text{ s}^{-1}$	3.2×10^{-3}	2.8×10^{-4}	9.0×10^{-5}
(8)	$\text{PtCl}_3\text{H}_2\text{O}^-$	H_2O	$(9.1 \pm 0.8) \times 10^{-3} \text{ s}^{-1}$	2.79×10^{-2}	9.1×10^{-3}	9.3×10^{-5}
(9a)	<u>trans</u> - $\text{PtCl}_2(\text{H}_2\text{O})_2$	H_2O	$(4.0 \pm 0.4) \times 10^{-3}$	-	2.0×10^{-3}	-
(9b)	<u>trans</u> - $\text{PtCl}_2(\text{H}_2\text{O})_2$	Cl^-	$(5.9 \pm 0.4) \times 10^{-3}$	1.42×10^{-3}	3.0×10^{-3}	7.0×10^{-3}
(10)	<u>cis</u> - $\text{PtCl}_2(\text{H}_2\text{O})_2$	H_2O	$(3.6 \pm 0.5) \times 10^{-2}$	2.53×10^{-2}	1.8×10^{-2}	1.3×10^{-2}
(11)	$\text{PtCl}(\text{H}_2\text{O})_3^+$	<u>trans</u> - H_2O	$(3.5 \pm 0.3) \times 10^{-2}$	1.2×10^{-2}	3.5×10^{-2}	3.6×10^{-2}
(12)	$\text{Pt}(\text{H}_2\text{O})_4^{2+}$	H_2O	$(1.0 \pm 0.1) \times 10^{-2}$	8.4×10^{-5}	2.5×10^{-3}	1.9×10^{-4}

[†] Green and Wilson³ obtained $(2.06 \pm 0.06) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$, $(9.1 \pm 1.1) \times 10^{-3} \text{ M}^{-1} \text{ s}^{-1}$ for reactions (7) and (8), respectively.

TABLE 3

Second-order rate constants for reaction of PtCl_4^{2-} with various olefins at 25 °C.

Olefin	$k_2 \times 10^3 / \text{M}^{-1} \text{ s}^{-1}$	Ionic medium	Ref.
$\text{CH}_2:\text{CH}_2$	1.1 ± 0.1	1M ClO_4^-	This paper
$\text{CH}_2:\text{CH} \cdot \text{CH}_2\text{OH}$	1.03 ± 0.02	2M Cl^-	2
$\text{CH}_2:\text{CH} \cdot \text{CH}_2\text{NH}_3^+$	1.86 ± 0.02	2M Cl^-	2
$\text{CH}_2:\text{CH} \cdot \text{CH}_2\text{SO}_3^-$	0.83 ± 0.02	2M Cl^-	2

TABLE 4

Comparison between the reactivity of the aqua complexes $\text{PtCl}_3(\text{H}_2\text{O})^-$ and $\text{PtCl}(\text{H}_2\text{O})_3^+$ and the corresponding chloro complexes, PtCl_4^{2-} and trans- $\text{PtCl}_2(\text{H}_2\text{O})_2$, respectively, for various entering ligands (Rate constants from Ref. 1 and the present study).

Substrate complex	Leaving ligand	$k/M^{-1} s^{-1}$					
		Cl^-	Br^-	I^-	SCN^-	DMSO	C_2H_4
PtCl_4^{2-}	Cl^-	$\sim 1 \times 10^{-5}$	4.8×10^{-5}	2.0×10^{-2}	0.010	3.2×10^{-3}	1.1×10^{-3}
$\text{PtCl}_3\text{H}_2\text{O}^-$	H_2O	5.2×10^{-3}	2.1×10^{-2}	0.38	0.10	2.8×10^{-2}	9.1×10^{-3}
<u>trans</u> - $\text{PtCl}_2(\text{H}_2\text{O})_2$	Cl^-	-	6.7×10^{-3}	0.31	0.30	1.42×10^{-3}	5.9×10^{-3}
$\text{PtCl}(\text{H}_2\text{O})_3^+$	<u>trans</u> - H_2O	0.46	1.7	39	16	1.2×10^{-2}	3.5×10^{-2}

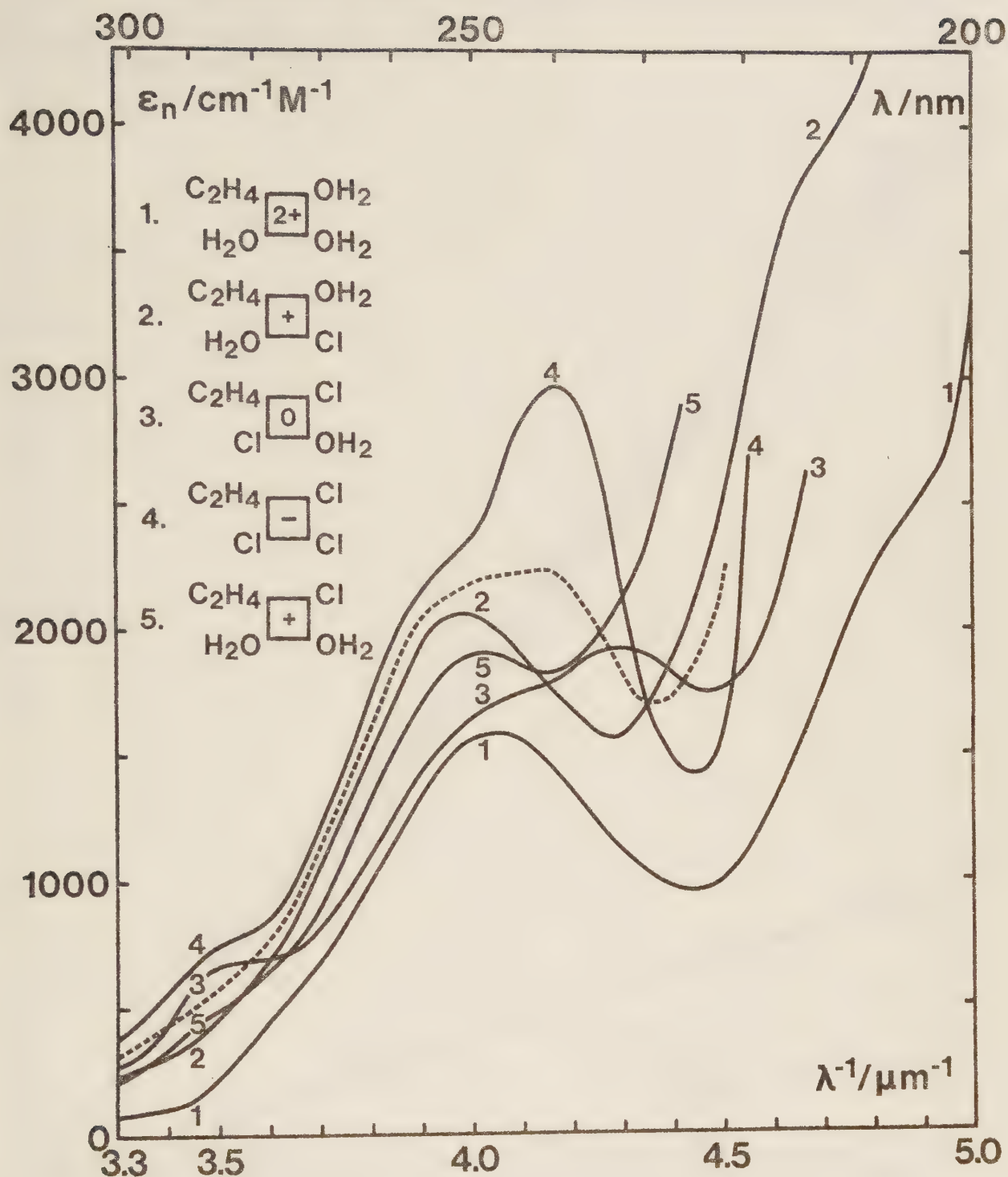


FIGURE 1. Spectra of the complexes 1 - $\text{Pt}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_3^{2+}$, 2 - trans - $\text{PtCl}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_2^+$, 3 - trans- $\text{PtCl}_2(\text{C}_2\text{H}_4)(\text{H}_2\text{O})$, 4 - $\text{PtCl}_3(\text{C}_2\text{H}_4)^-$ and 5-cis- $\text{PtCl}(\text{C}_2\text{H}_4)(\text{H}_2\text{O})_2^+$. The dashed spectrum was recorded using an equilibrated solution of reaction (9) with $\underline{C}_{\text{Pt}} = 1.09 \times 10^{-4} \text{ M}$, $[\text{C}_2\text{H}_4] = 5.0 \text{ mM}$, and $[\text{Cl}^-] = 50 \text{ mM}$. It is a superposition of spectra 2 and 4 in the ratio $(1.5 \pm 0.2):1$.

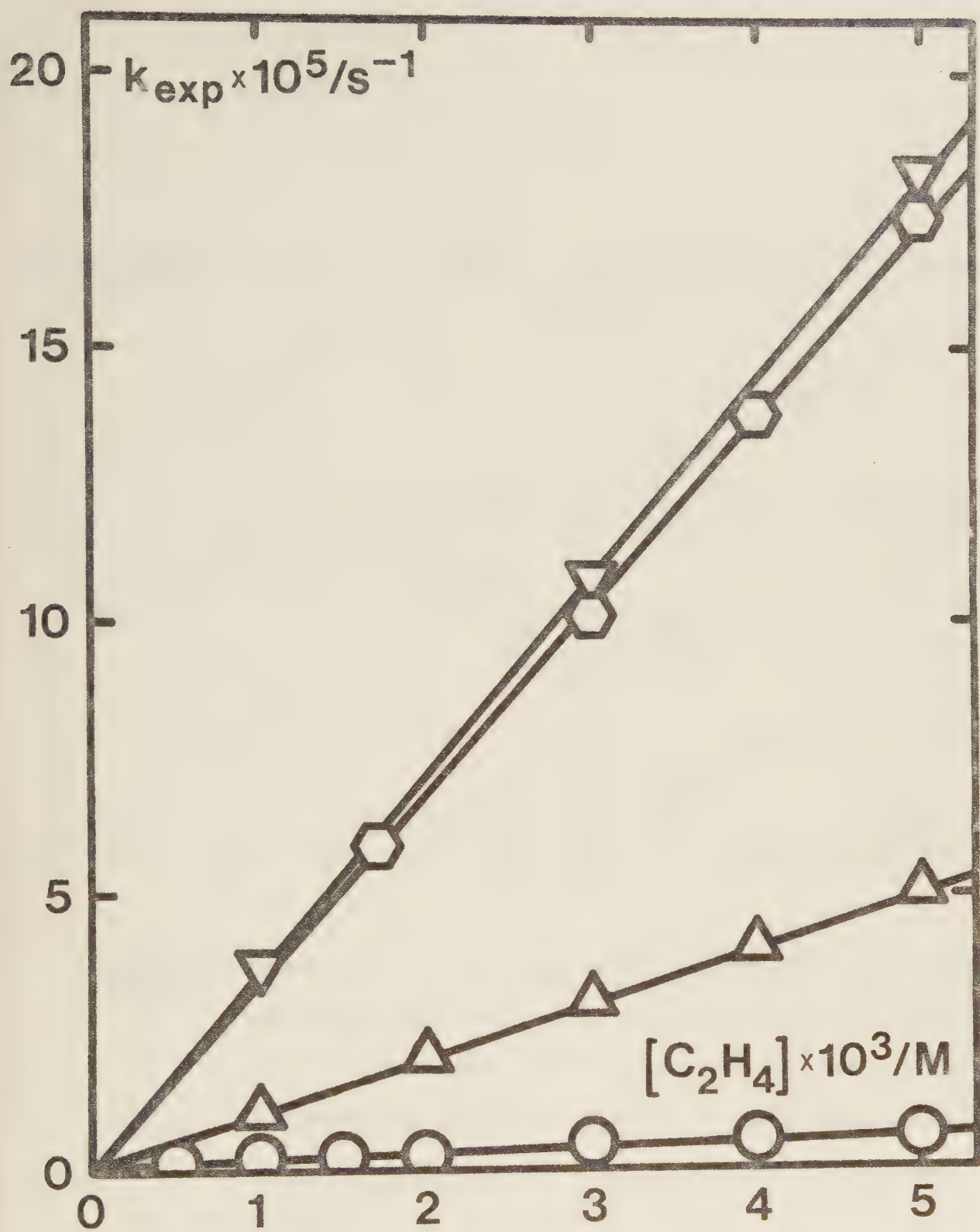


FIGURE 2. Observed rate constants for reactions (7)- $\circ$; (10)- ∇ ; (11)- $\hexagon$ and (12)- $\triangle$ vs. the concentration of excess ethene.

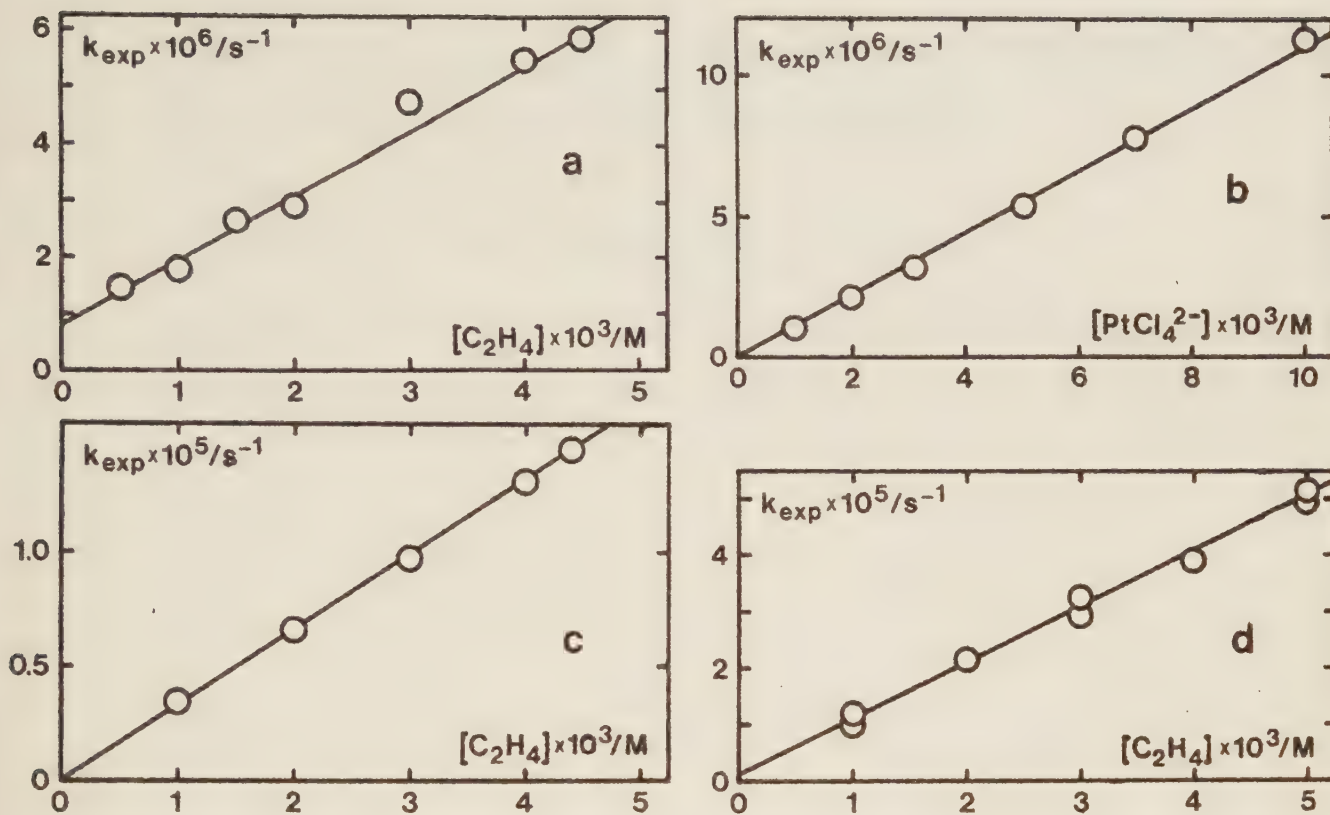


FIGURE 3. Observed rate constants for reactions (7), (8) and (9) vs. concentration of excess reactant, (a) - reaction (7) for excess ethene, (b) - reaction (7) for excess tetrachloroplatinate(II), (c) - reaction (8) for excess ethene and (d) - reaction (9) for excess ethene.

Kinetics and Mechanism for the Reaction between Tetrachloro
and Tetrabromo Aurate(III) and Thiocyanate

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The kinetics and mechanism for the over-all reaction ($X=\text{Cl}, \text{Br}$)



have been studied at 25.0 °C using stopped-flow spectrophotometry.

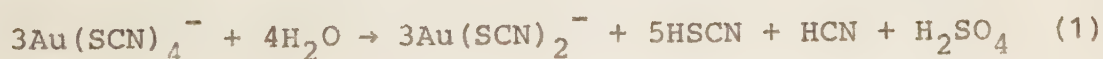
The initial, rapid process can be identified as stepwise ligand substitutions ($\underline{n}=0,1,2,3,4$)



which take place via direct displacements, the solvent path being negligible. The substitution kinetics give no evidence for formation of persistent five-coordinate intermediates, which has been suggested in the literature. The rate of the subsequent slower reduction of gold(III) to gold(I) thiocyanato species varies four orders of magnitude within the accessible concentration interval of gold. The slow rates at high gold concentrations are due to inhibition by the cyanide formed in the redox step. The inhibition is eliminated for gold concentrations smaller than $5 \times 10^{-6} \text{ M}$, where the redox reaction is rapid and strictly first-order with respect to thiocyanate. The mechanism for the reductive elimination is intermolecular, involving a reaction between the Au(III) complex and an outer-sphere thiocyanate. For $[\text{SCN}^-] > 5 \text{ mM}$, the experiments indicate that higher thiocyanato complexes of gold(III) might be formed.

INTRODUCTION

N. Bjerrum and Aa. Kirschner¹ showed already in 1918 that both gold(III) and gold(I) thiocyanato complexes are spontaneously reduced in aqueous solution to metallic gold. Especially, they studied the stoichiometry and kinetics for the redox process (1)



which was a relatively slow reaction with a half-life of the order of hours and with no simple-order kinetics with respect to gold for the experimental conditions used. Very little has been published about gold-thiocyanato complexes since this classical paper appeared 60 years ago. A few thermodynamic studies^{2,3,4,5} have confirmed or only slightly revised B & K's conclusions about stabilities and standard potentials. Some qualitative observations^{2,3} about the reduction rates of $\text{Au}(\text{SCN})_4^-$ according to (1) and a kinetic study⁶ of the reduction of AuBr_4^- by thiocyanate have appeared. The latter gave no clues to the mechanism.

For the preparation of $\text{Au}(\text{SCN})_4^-$, Bjerrum and Kirschner¹ used the reaction between tetrachloroaurate(III) and thiocyanate, which was complete within the time of mixing ($\text{X}=\text{Cl}$):



Hall and Satchell⁷ have recently studied the kinetics in this system ($\text{X}=\text{Cl}$) using stopped-flow spectrophotometry. They observed two consecutive processes, and suggested a mechanism, according to which the initial rapid process was due to the formation of a long-lived five-coordinate intermediate, $\text{AuCl}_4^- \cdots \text{SCN}^-$, and the subsequent, slower one, to the rearrangement of this intermediate to $\text{AuCl}_3\text{SCN}^-$ and Cl^- . Subsequent substitutions to $\text{Au}(\text{SCN})_4^-$ were assumed to be negligible for the experimental conditions used. A reduction to Au(I) by thiocyanate was also considered less probable, since the early studies^{1,2} had shown the reduction to be relatively slow.

The same type of mechanism was also used by H & S to describe the observed kinetics for the reaction between tetrachloroaurate(III) and bromide. In that case, however, a recent study⁸ has shown that H & S's results should more likely be

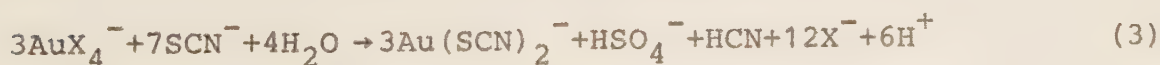
interpreted as consecutive ligand substitutions. The existence of persistent five-coordinate intermediates in the AuCl_4^- -bromide system is not very likely.

It is well-known that gold(III) complexes are easily reduced to gold(I) by ligands with reducing properties. Most of these reductions are reported to proceed by an initial substitution followed by a rapid electron transfer. Both intramolecular and intermolecular mechanisms for the redox process have been suggested. For instance, the reduction of tetrachloroaurate(III) with various carboxylic acid derivatives has been postulated to involve a rapid intramolecular two-electron transfer between the carboxylic ligand and the metal.⁹ On the other hand, the mechanism for the reaction between $\text{Au}(\text{NH}_3)_4^{3+}$ and thiosulfate involves initial complex formation followed by an intermolecular reduction by an outer-sphere thiosulfate.¹⁰ An intermolecular mechanism has also been proposed for the reduction of Au(III) complexes by methionine.¹¹

Under these circumstances, a detailed study of the reaction mechanisms for both the ligand substitution and redox reactions in the AuX_4^- -thiocyanate systems ($\text{X}=\text{Cl}, \text{Br}$) was desirable.

SURVEY OF THE SYSTEM

For concentrations of gold smaller than ca. 5×10^{-6} M, the concentration of cyanide formed in the reduction is so small that formation of Au(III) cyanide complexes can be neglected. A combination of (1) and (2) gives the over-all reaction (3), $\text{X}=\text{Cl}, \text{Br}$:



Addition of excess thiocyanate to solutions of AuCl_4^- or AuBr_4^- ($\text{C}_{\text{Au}} < 5 \times 10^{-6}$ M) reveals two kinetically well separated reactions in

agreement with H & S's observations.⁷ For $C_{\text{Au}} < 10^{-5}$ M, both these reactions are strictly first-order with respect to thiocyanate. The initial fast step can be identified as a substitution of the halide ligands by thiocyanate and the subsequent process as a reduction of Au(III) complexes to Au(I) contrary to H & S's interpretation.⁷ Both reactions have half-lives within the stopped-flow-region but the substitution is always at least ten times faster than the reduction, so they can be studied independently of each other.

Ligand Substitution Equilibria. The equilibrium constants (4); $\underline{n}=0,1,2,3$; $X=\text{Cl},\text{Br}$.

$$\underline{K}_{\underline{n}} = \frac{[\text{AuX}_{3-\underline{n}}(\text{SCN})_{\underline{n}+1}^-][X^-]}{[\text{AuX}_{4-\underline{n}}(\text{SCN})_{\underline{n}}^-][\text{SCN}^-]} \quad (4)$$

for the stepwise processes (5)



are related to the over-all stability constants (6) for the simple systems

$$\underline{\beta}_{4X} = \frac{[\text{AuX}_4^-]}{[\text{Au}^{3+}][X^-]^4} \quad (6)$$

by the relation (7)

$$\underline{K}_0 \underline{K}_1 \underline{K}_2 \underline{K}_3 = \underline{\beta}_{4\text{SCN}} / \underline{\beta}_{4X} \quad (7)$$

Skibsted and Bjerrum¹² have calculated $\underline{\beta}_{4\text{Cl}} = 10^{26} \text{ M}^{-4}$, $\underline{\beta}_{4\text{Br}} = 10^{34} \text{ M}^{-4}$ and $\underline{\beta}_{4\text{SCN}} = 10^{45} \text{ M}^{-4}$. If we assume that the distribution of gold between the various mixed species $\text{AuX}_{4-\underline{n}}(\text{SCN})_{\underline{n}}^-$, $\underline{n}=0,1,2,3$, 4 is approximately statistical (cf. Ref. 8), we can calculate

the equilibrium constants (4) and from them a tentative distribution of gold for various ratios $[\text{SCN}^-]/[\text{X}^-]$ using standard methods,¹³ see Figure 1. The experimentally accessible region for the kinetic experiments is indicated in the Figure. The lower limit in order to assure first-order kinetics is $[\text{SCN}^-]/[\text{X}^-] > \text{ca. } 5 \times 10^{-5}$ for both systems.

Figure 1 shows directly that $\text{Au}[\text{SCN}]_4^-$ will be the predominant reaction product in the fast substitution process for the ratios $[\text{SCN}^-]/[\text{Cl}^-] \geq 3 \times 10^{-3}$ used by H & S,⁷ not $\text{AuCl}_3\text{SCN}^-$ as suggested by these authors.

Spectra. - Figure 2 shows spectra of solutions containing equilibrium mixtures of the thermodynamically unstable complexes $\text{AuX}_{4-n}(\text{SCN})_n^-$; $n=0,1,2,3,4$ recorded using a flow cell before any significant reduction to Au(I) has occurred. A comparison of these spectra with the distribution diagram in Figure 1 shows that already for the lowest ratio $[\text{SCN}^-]/[\text{X}^-] = 5 \times 10^{-5}$ the main part of the gold will probably be present as $\text{AuCl}(\text{SCN})_3^-$ and $\text{Au}(\text{SCN})_4^-$ in the chloro-thiocyanato system, whereas in the bromo-thiocyanato system, all the various mixed complexes will contribute to the over-all absorbance. The limiting curve for high concentrations of thiocyanate (ref. 1) can be identified as the spectrum for $\text{Au}(\text{SCN})_4^-$.¹⁴ The rapid increase of absorbance that can be observed at 312 nm is therefore due to the stepwise substitutions (5).

Substitution Kinetics. - The experiments indicate that the reaction model in Figure 3 can be used to describe the over-all process (2), cf. the analogous $\text{AuCl}_4^- - \text{Br}^-$ and $\text{PtCl}_4^{2-} - \text{Br}^-$ systems.^{8,15} The large difference in trans-effect between halides and thiocyanate makes the reaction via the cis-isomer negligible. Because of the rapid subsequent redox process, it has been possible to study only some of the stepwise substitutions indicated

by the scheme, viz. reactions (8), (9), and (10):



Redox Kinetics. - The redox reaction can be followed as a decrease of absorbance at 312 nm where all the reaction products in (3) have a negligible absorbance compared to the $\text{AuX}_{4-n}(\text{SCN})_n^-$ -complexes, cf. Figure 2.

The redox rate varies by a factor of about four orders of magnitude with the total concentration of gold(III) for $\underline{C}_{\text{Au}} > 5 \times 10^{-6}$ M. This is illustrated by Figure 4, where the redox rate constants (or estimated constants, when the kinetics have deviated from first-order) from various studies have been plotted vs. $\underline{C}_{\text{Au}}$ in a logarithmic scale. This large variation in rate has been overlooked in previous studies. The kinetics deviate from simple first-order for $\underline{C}_{\text{Au}} > \underline{\text{ca.}} 10^{-5}$ M. The deviations are very large for the high gold concentrations that had to be used by B & K (see Ref. 1 p. 8). The variation of the rate constants with the gold concentration is also shown by the plots in Figure 5, where the two curves for 1.25×10^{-5} M and 5×10^{-5} M gold(III) deviate from the two with smaller gold(III) concentrations.

This strong gold(III) dependence cannot be explained by inhibition by the Au(I) formed. The reduction is rapid and complete for $\underline{C}_{\text{Au}} \leq 5 \times 10^{-6}$ M. The experiments in Table 1 show that addition of cyanide-free $\text{Au}(\text{SCN})_2^-$ prepared by reduction of AuCl_4^- with sulfite and subsequent addition of thiocyanate does not change the rate constants. On the other hand, addition of cyanide to the reaction mixture inhibits the reaction

strongly * and causes deviations from first-order kinetics. Au(I) prepared according to (3) by reduction of AuCl_4^- ($C_{\text{Au}} > 10^{-5} \text{ M}$) with thiocyanate has a similar effect, cf. Table 1.

From these observations we conclude that the cyanide formed in the redox process (3) inhibits the reaction, probably by a rapid coordination to Au(III). Even for large concentrations of Au(III) (10^{-4} to 10^{-3} M), kinetic experiments show a very fast initial reduction of part of the gold. The cyanide formed during this initial period of the kinetics can rapidly coordinate to the unchanged Au(III), which will cause a gradual decrease of the reduction rate and deviations from first-order kinetics. (Gold(III)-cyanide complexes are reduced very slowly by thiocyanate).

For the small concentrations of gold used in the present study ($C_{\text{Au}} < 5 \times 10^{-6} \text{ M}$) this effect of cyanide is eliminated, probably due to kinetic reasons. The rate of substitution of the thiocyanate in $\text{Au}(\text{SCN})_4^-$ by cyanide will probably be small compared to the reduction rate for cyanide concentrations about 10^{-6} M . From the thermodynamic point of view, the cyanido complexes will be more stable than the thiocyanato complexes, ($\beta_{4\text{CN}}/\beta_{4\text{SCN}} \approx \approx 10^{37}$ cf. Ref. 12) even for these low concentrations of cyanide.

EXPERIMENTAL

Chemicals and solutions. - Hydrogen tetrachloroaurate(III) trihydrate, $\text{HAuCl}_4 \cdot 3\text{H}_2\text{O}$ (Mallinckrodt or Degussa) was used directly.

* Already B & K (Ref. 1, p. 16) observed, that cyanide influenced the redox rate. They observed a rapid decoloration of the red $\text{Au}(\text{SCN})_4^-$ when excess cyanide was added. The change was assumed to be due to a rapid reduction, but is more likely a rapid formation of $\text{Au}(\text{CN})_4^-$.

1.00 M stock solutions were prepared from perchloric acid (Baker's p.a.), sodium perchlorate (Baker's p.a.), sodium chloride (Merck's p.a.), sodium bromide (Mallinckrodt's p.a.), sodium thiocyanate (Mallinckrodt's p.a.) and water, doubly distilled from quartz vessels. Stock solutions of potassium cyanide (B.D.H. p.a.) were 0.010 M.

Solutions of tetrabromoaurate(III) were prepared by addition of sodium bromide to solutions of tetrachloroaurate in such concentrations that the quotient $[\text{Br}^-]/[\text{Cl}^-] \geq 10$ (cf. Ref. 8). Gold(I)-solutions were prepared either by reduction of AuCl_4^- with excess thiocyanate according to (3) or by reduction of AuCl_4^- with sodium bisulfite (Merck's p.a.) in a five-percent deficit and subsequent rapid addition of excess thiocyanate.

Stoichiometry. - The stoichiometry of reaction (1) was carefully studied by Bjerrum and Kirschner.¹ We checked the sulphate analyses for the small concentrations of gold ($< 5 \times 10^{-5}$ M) used in the present study by precipitation from large volumes of the sulfate formed in reaction (3) with barium. Comparisons with standards showed that the ratio $[\text{gold(III)}]/[\text{sulphate}]$ was 3.0 ± 0.1 in agreement with Ref. 1. After the reduction, the Au(I) will be present as $\text{Au}(\text{SCN})_2^-$ for the experimental conditions used (cf. the stability constants for Au(I) complexes given by Skibsted and Bjerrum and $\text{p}K_{\text{aH}^+\text{CN}} = 9.40$).

Spectra. - The spectra in Figure 2 were recorded using a Beckman Model 25 recording instrument and a continuous-flow system with a dead-time much smaller than the redox half-lives of the complexes.

Kinetics. - All reactions were started by mixing equal volumes of a metal solution (M) and a ligand solution (L) at $(25.00 \pm 0.02)^\circ\text{C}$. The change of absorbance at 312 nm was followed using a modified Durrum-Gibson stopped-flow instrument. The ab-

sorbance first rapidly increases due to the substitutions (5) and then slowly decreases due to the reduction (cf. Fig. 2). The metal solution (M) contained gold(III) ($C_{\text{Au}} \leq 1.0 \times 10^{-5} \text{ M}$) with varying concentrations of chloride and bromide. The ligand solution (L) contained thiocyanate and in experiments with large halide concentrations, chloride or bromide also. For the experiments in Table 1, the L-solution contained Au(I) or cyanide also.

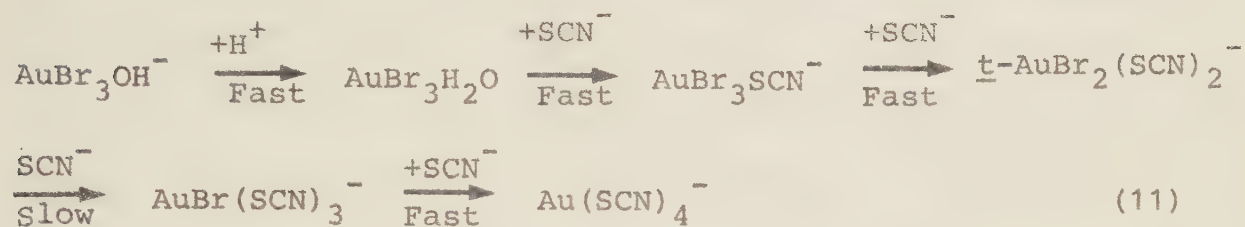
Tables 1-3 give the concentrations after mixing, all solutions having the ionic strength 1.00 M with sodium perchlorate as the supporting electrolyte. The hydrogen ion concentration was varied within the interval $0.2 \text{ mM} \leq [\text{H}^+] \leq 20 \text{ mM}$ by substitution of part of the sodium perchlorate of the M-solution by perchloric acid. This variation had no influence on the reaction rates. The formation of HSCN was negligible ($\text{p}K_{\text{a}} = -1.8$)¹⁶ For $[\text{H}^+] > 0.1 \text{ M}$ side reactions due to decomposition of thiocyanate disturb the kinetics.

Large excess of thiocyanate, chloride, bromide, gold(I) and cyanide compared to gold(III) complex gave pseudo first-order kinetics. Reverse processes were negligible, except for reaction (8). Rate constants were calculated from first-order rate expressions using a least-squares programme and a computer.

Substitution. - The experiments are reviewed in Table 2. The reversible reaction (8) was started by mixing an M-solution having $C_{\text{Au}} = 1 \times 10^{-5} \text{ M}$, $C_{\text{Br}} = 0.990 \text{ M}$ or 0.500 M and $C_{\text{H}^+} = 0.010 \text{ M}$ with L-solutions containing sodium thiocyanate (0.10, 0.15, 0.20, 0.30, 0.40, 0.50, 0.80 or 1.2 mM) in 1.00 M sodium bromide and (0.10, 0.15, 0.20, 0.30, 0.40 or 0.50 mM) in 1.00 M sodium perchlorate solution. The reaction product in these runs was mainly $\text{AuBr}_3\text{SCN}^-$ - cf. Fig. 1.

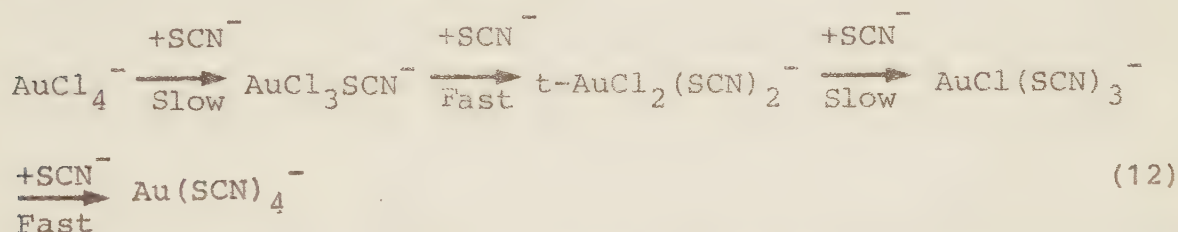
Reaction (9) was followed by mixing a L-solution having $C_{\text{SCN}} 2.0, 4.0$ or 8.0 mM and $C_{\text{H}^+} = 2.0 \text{ mM}$ with a M-solution con-

taining 1×10^{-5} M AuBr_3OH^- in 1.00 M NaClO_4 . The latter was prepared by addition of one equivalent of sodium hydroxide to a 0.1 mM AuBr_4^- -solution in 1.00 M sodium perchlorate. After mixing, the following reactions take place:



The preceding fast reactions are complete within less than one half-life of the slow process, and the subsequent reaction $\text{AuBr}(\text{SCN})_3^- \rightarrow \text{Au}(\text{SCN})_4^-$ is fast because of the large trans-effect of SCN^- compared to Br^- .

Reaction (10) was followed by mixing an M-solution having $C_{\text{Au}} = 1 \times 10^{-5}$ M, $C_{\text{Cl}} = 0.200$ M and $C_{\text{H}^+} = 0.020$ M with L-solutions of sodium thiocyanate (1.0, 2.0, 4.0, 6.0, 8.0 or 10.0 mM). After mixing, the following reactions take place:



Reaction (10) can be observed as a fast initial process followed by the slower reaction between trans- $\text{AuCl}_2(\text{SCN})_2^-$ and thiocyanate. Reaction (10) might be disturbed by the subsequent reaction between trans- $\text{AuCl}_2(\text{SCN})_2^-$ and thiocyanate.

Redox reactions. - The explanatory experiments in Table 1 and Figures 4 and 5 showed that simple first-order kinetics is obtained and the gold(III) dependence is eliminated for $C_{\text{Au}} \leq 5 \times 10^{-6}$ M. The experiments reviewed in Table 3 were performed at constant ratios $[\text{SCN}^-]/[\text{X}^-]$, $\text{X} = \text{Cl}$ or Br , and thus constant distribution of the gold between the different complexes, cf. Fig. 1. The M-solution contained AuCl_4^- and sodium chloride or AuBr_4^- and sodium bromide and the L-solution sodium thio-

cyanate in a chloride- or a bromide-perchlorate medium.

The reaction for $\bar{n}_{\text{SCN}}=4$ was started either by addition of thiocyanate (2.0, 6.0 and 10.0 mM) to a solution of AuCl_4^- ($C_{\text{Au}}=1.0 \times 10^{-5}$ M, $C_{\text{Cl}}=0.200$ M, $C_{\text{H}^+}=20$ mM) or by addition of sodium thiocyanate (1.0, 2.0, 4.0 or 6.0 mM) to a solution of AuBr_4^- ($C_{\text{Au}}=1.0 \times 10^{-5}$ M, $C_{\text{Br}}=1 \times 10^{-3}$ M, $C_{\text{H}^+}=10$ mM. The quotient $[\text{SCN}^-]/[\text{X}]$ $\text{X}=\text{Cl}, \text{Br}$, was 0.01 (Cl^-) or ≥ 1 (Br^-). The start complex for the reduction in these runs was $\text{Au}(\text{SCN})_4^-$ - cf. Figure 1.

The reduction for $[\text{SCN}^-]>5$ mM - see Figure 5 - was started by mixing an M-solution containing $C_{\text{Au}} 1 \times 10^{-5}$ M or 5×10^{-6} M, $C_{\text{Cl}}=0.200$ M with an L-solution of sodium thiocyanate (0.020, 0.040, 0.060, 0.080, 0.100, 0.200, 0.400, 0.600, 0.800, 1.000).

As observed by Hall and Satchell⁷ also, there is a very small chloride dependence of the redox rate. The experiments reviewed in Figure 6 were started by mixing an M-solution having $C_{\text{Au}}=1.0 \times 10^{-5}$ M, $C_{\text{Cl}}=0.200, 0.600$ or 1.00 M and $C_{\text{H}^+}=0.020$ M with an L-solution of sodium thiocyanate having $C_{\text{SCN}}=0.100, 0.200, 0.500, 1.00, 2.00, 10.0, 14.0, 20.0, 40.0, 60.0, 100$ mM and, for the experiments with the chloride concentration 0.950 M after mixing, 0.900 M sodium chloride also.

RESULTS AND DISCUSSION

Substitution. - The stepwise substitutions (8), (9) and (10) take place via a direct ligand exchange. Similar to the AuCl_4^- -bromide system,⁸ the solvent path is negligible. Using the notations for the rate constants in Figure 3, the observed first-order rate constant for excess thiocyanate and bromide for reaction (8) can be written

$$k_{\text{exp}} = k_{0\text{SCN}}^{\text{Br}} [\text{SCN}^-] + k_{0\text{Br}}^{\text{Br}} [\text{Br}^-] \quad (13)$$

Figure 7a shows plots of the observed rate constant vs. the thiocyanate concentration at three different bromide concentrations. According to eqn. (13), the slopes give k_{0SCN}^{Br} and the intercept $k_{0Br}^{Br}[Br^-]$. Figure 7b shows a plot of the intercept vs. $[Br^-]$ which gives k_{0Br}^{Br} as the slope.

Reactions (9) and (10) were studied using a large excess of thiocyanate so the reverse reactions were suppressed. The experimental rate constants are given by eqns. (14) and (15)

$$k_{exp} = k_{2tSCN}^{Br} [SCN^-] \quad (14)$$

$$k_{exp} = k_{0SCN}^{Cl} [SCN^-] \quad (15)$$

Figures 7c and d show the plots according to these eqns. The slopes give k_{2tSCN}^{Br} and k_{0SCN}^{Cl} , respectively.

The rate constants are given in Table 4 together with the statistically corrected values. A comparison of k_{0SCN}^{Br} and k_{2tSCN}^{Br} shows that the relative cis-effect Br^-/SCN^- is about 2. The values for k_{0SCN}^{Br} and k_{0SCN}^{Cl} show that the relative trans-effect Br^-/Cl^- is 8 for thiocyanate as entering ligand, which should be compared to the value 14 obtained previously⁸ for chloride and bromide as entering ligands. Thus, the relative trans-effect depends on the nature of the entering ligand for gold(III) complexes. We have previously shown¹⁷ that this is valid for the platinum(II) complexes also.

The equilibrium constant $K_0 = \frac{k_{0SCN}^{Br}}{k_{0Br}^{Br}} = (6.2 \pm 0.7) \times 10^3$ for reaction (8) can be obtained from the kinetics, and might be compared with the statistical estimation 2.3×10^3 .

Reduction. - For an intramolecular redox process, the rate should be independent of the concentration of free thiocyanate for constant distribution of gold between the various complexes $AuX_{4-n}(SCN)_n^-$, $n=0,1,2,3,4$. The distribution is determined by

the ratios $[\text{SCN}^-]/[\text{X}^-]$, cf. Figure 1 and eqn. (4). For an intermolecular process, on the other hand, the redox rate should be proportional to the concentration of free thiocyanate for constant ratios $[\text{SCN}^-]/[\text{X}^-]$.

Figure 8 shows plots of the experimental rate constants vs. the concentration of thiocyanate for the experiments with constant ratios $[\text{SCN}^-]/[\text{X}^-]$. Obviously, the observed rate constants are proportional to the concentration of free thiocyanate for $[\text{SCN}^-] \leq 5 \text{ mM}$, which supports the intermolecular mechanism, i.e. an attack on the complex by an outer-sphere thiocyanate. The stoichiometric reaction mechanism in Figure 9, where k_r^X denotes reduction rate constants, can be used to describe the kinetics. In principle, each of the complexes $\text{AuX}_{4-n}(\text{SCN})_n^-$, $n=0,1,2,3,4$ in rapid equilibrium with each other, can be reduced by thiocyanate, so the over-all rate can be written

$$\text{Rate} = \left(\sum_{i=0}^4 k_{ri}^X [\text{AuX}_{4-i}(\text{SCN})_i^-] \right) \times [\text{SCN}^-] \quad (16)$$

which gives the experimental first-order rate constant (17)

$$k_{\text{exp}} = \frac{k_{r0}^X + k_{r1}^X \times \beta_1 \times Q + k_{r2}^X \times \beta_2 \times Q^2 + k_{r3}^X \times \beta_3 \times Q^3 + k_{r4}^X \times \beta_4 \times Q^4}{1 + \sum_{i=1}^4 \beta_i Q^i} \times [\text{SCN}^-] \quad (17)$$

$$\text{or } k_{\text{exp}} = \left(\sum_{i=0}^4 \alpha_i k_{ri}^X \right) \times [\text{SCN}^-] \quad (18)$$

where $Q = [\text{SCN}^-]/[\text{X}]$, β_i are stability constants defined by eqn. (19),

$$\beta_{j+1} = \prod_{i=0}^j K_i, \quad j=0,1,2,3 \quad (19)$$

and α_n denotes the fraction of gold present as $\text{AuX}_{4-n}(\text{SCN})_n^-$. Thus, the observed redox rate constants are in principle sums of rate constants, k_{rn} , $n=0,1,2,3,4$ for the parallel paths of

The experiments show that the reverse redox reaction is negligible. This might be due to thermodynamic reasons (cf. the reaction $\text{AuI}_4^- \rightleftharpoons \text{AuI}_2^- + \text{I}_2^{22}$). Calculations using standard potentials⁶ also show that the reduction is completely displaced towards gold(I) at the concentrations of gold(III) and thiocyanate used. Another reason might be that the species (LSCN) and $(\text{SCN})_2$ are rapidly decomposed by water.^{20,23,24} All attempts to detect them in aqueous solutions using stopped-flow techniques have failed.

Also for large concentrations of thiocyanate ($\text{SCN}^- > 5 \text{ mM}$) the experiments show that an intermolecular mechanism must be considered. The experiments in Figure 5 might indicate formation of higher thiocyanato complexes, for instance $\text{Au}(\text{SCN})_5^{2-}$ and $\text{Au}(\text{SCN})_6^{3-}$, having tentative stability constants of about 170 M^{-1} and 100 M^{-2} respectively, and slow reduction rates. The mechanism for the redox process in this interval of thiocyanate concentration will be the subject of further study.

Acknowledgements

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Figure Captions

Figure 1. The distribution of gold between the species $\text{AuX}_{4-\underline{n}}(\text{SCN})_{\underline{n}}^-$, $\underline{n}=0,1,2,3,4$; $\text{X}=\text{Cl}, \text{Br}$, calculated from the β_4 values in Ref. 12 and assuming a statistical distribution of the gold. The arrows denote experimentally accessible regions.

Figure 2. Flow spectra of solutions containing equilibrium mixtures of the thermodynamically unstable complexes $\text{AuX}_{4-\underline{n}}(\text{SCN})_{\underline{n}}^-$, $\underline{n}=0,1,2,3,4$; $\text{X}=\text{Cl}$ (a), $\text{X}=\text{Br}$ (b).

Figure 3. Reaction model for the substitutions. The reaction via the cis-isomer is negligible because of the large difference in trans-effect between X^- and SCN^- .

Figure 4. The observed rate constant for the reduction as a function of $\underline{C}_{\text{Au}}$ in a logarithmic scale.
 $\underline{C}_{\text{Au}}=2.5 \times 10^{-6} \text{ M}$, $5 \times 10^{-6} \text{ M}$, $1.25 \times 10^{-5} \text{ M}$ and $5 \times 10^{-5} \text{ M}$
 with $\underline{C}_{\text{SCN}}=0.100 \text{ M}$, ($\bigcirc$), or 0.01 M , ($\square$), $\underline{C}_{\text{Cl}}=0.100 \text{ M}$
 and $\underline{C}_{\text{H}^+}=10 \text{ mM}$. The value from ref. 7 with $\underline{C}_{\text{Au}}=4 \times 10^{-5} \text{ M}$,
 $\underline{C}_{\text{SCN}}=10 \text{ mM}$, $\underline{C}_{\text{Cl}}=0.100 \text{ M}$ and $\underline{C}_{\text{H}^+}=2 \text{ mM}$ ($\blacksquare$) and estimated
 values from ref. 6 with $\underline{C}_{\text{Pt}} \approx 8 \times 10^{-5} \text{ M}$ and $\underline{C}_{\text{SCN}}=10 \text{ mM}$ and
 from ref. 1 with $\underline{C}_{\text{Pt}} 2 \times 10^{-3} \text{ M}$ and $4 \times 10^{-3} \text{ M}$, $\underline{C}_{\text{SCN}} \sim 100 \text{ mM}$
 are also included in the Figure.

Figure 5. The observed rate constant for the reduction of AuCl_4^-
vs. the thiocyanate concentration for large concentra-
 tions of thiocyanate. $\underline{C}_{\text{Cl}}=0.100 \text{ M}$,
 $\underline{C}_{\text{Au}}=2.5 \times 10^{-6} \text{ M}$ ($\triangle$), $5 \times 10^{-6} \text{ M}$ ($\bigcirc$), $1.25 \times 10^{-5} \text{ M}$ ($\square$)
 and $5 \times 10^{-5} \text{ M}$ ($\bigcirc$).

Figure 6. The observed rate constant for the reduction of AuCl_4^- by thiocyanate as a function of the chloride concentration for various thiocyanate concentrations.

Figure 7. Plots of the observed rate constants vs. the concentration of thiocyanate for the substitution reactions (8)-a, (9)-(c) and (10)-d. In (b), the intercepts from Fig. 7a have been plotted vs. $[\text{Br}^-]$.

Figure 8. The observed rate constant for the reduction of Au(III) by thiocyanate as a function of the thiocyanate concentration at constant ratios $[\text{SCN}^-]/[\text{X}^-]$.

Figure 9. Reaction model for the redox reaction. $\underline{K}_n$, $n=0,1,2,3$ denote the stepwise equilibrium constants for the processes (5). $\underline{k}_{r\ n}^X$, $n=0,1,2,3,4$ and $X=\text{Cl}, \text{Br}$ denote the reduction rate constants for the various complexes $\text{AuX}_{4-n}(\text{SCN})_n^-$.

Table 1. Variation of reduction rate constant with the concentrations of AuCl_4^- , Au(I) and CN^- :

$10^3[\text{SCN}^-]/\text{M}$	$10^6[\text{AuCl}_4^-]/\text{M}$	pH	$k_{\text{exp}}/\text{s}^{-1}$	Added substance
50	5.0	2.0	18 ± 2	$6.5 \times 10^{-4} \text{M Au(SCN)}_2^{\text{a}}$
50	5.0	2.0	18 ± 2	-
100	5.0	2.0	21 ± 2	$6.5 \times 10^{-4} \text{M Au(SCN)}_2^{\text{a}}$
100	5.0	2.0	22 ± 2	-
300	5.0	2.0	23 ± 2	$6.5 \times 10^{-4} \text{M Au(SCN)}_2^{\text{a}}$
300	5.0	2.0	24 ± 2	-
50	1.0	3.0	15 ± 2	$1.0 \times 10^{-5} \text{M Au(I)}^{\text{b}}$
50	5.0	2.0	2.1 ± 0.2	$3.5 \times 10^{-4} \text{M Au(I)}^{\text{b}}$
465	5.0	2.0	1.8 ± 0.2	$3.5 \times 10^{-4} \text{M Au(I)}^{\text{b}}$
500	1.0	~ 9	No reduction	$1.0 \times 10^{-4} \text{M NaCN}$
100	1.0	~ 9	9 ± 1	$2.5 \times 10^{-5} \text{M NaCN}$
100	1.0	~ 8	17 ± 3	$1.0 \times 10^{-5} \text{M NaCN}$

^a Prepared by reduction of AuCl_4^- with HSO_3^- and subsequent addition of excess NaSCN .

^b Prepared by reduction of AuCl_4^- with SCN^- according to reaction (3).

Table 2. Substitution kinetics. Reactions (8), (9) and (10). Wavelength 312 nm. $C_{Au}=5 \times 10^{-6}$ M, $[H^+]=5 \times 10^{-3}$ M.

Reaction	$10^4 C_{SCN}/M$	C_X/M	k_{exp}/s^{-1}
(8)	0.50	0.995	18 ± 1
<u>X=Br</u>	0.75	0.995	21 ± 1
	1.0	0.995	22 ± 1
	1.5	0.995	27 ± 1
	2.0	0.995	34 ± 2
	2.5	0.995	37 ± 2
	4.0	0.995	49 ± 2
	6.0	0.995	63 ± 3
	0.50	0.750	16 ± 1
	0.75	0.750	19 ± 1
	1.0	0.750	19 ± 1
	1.5	0.750	25 ± 1
	2.0	0.750	29 ± 1
	2.5	0.750	34 ± 1
	0.50	0.495	12 ± 1
	0.75	0.495	13 ± 1
	1.0	0.495	15 ± 1
	1.5	0.495	20 ± 1
	2.0	0.495	24 ± 2
	2.5	0.495	28 ± 2
(9)	10.0	-	10 ± 2
<u>X=Br</u>	20.0	-	22 ± 2
	40.0	-	46 ± 3
(10)	5.0	0.100	8 ± 1
<u>X=Cl</u>	10.0	0.100	14 ± 1
	20.0	0.100	25 ± 2
	30.0	0.100	40 ± 3
	40.0	0.100	52 ± 5
	50.0	0.100	67 ± 7

Table 3. Redox kinetics. $C_{Au} = 5 \times 10^{-6} \text{ M}$, $[H^+] = 5 \times 10^{-3} \text{ M}$.
Wavelength 312 nm.

$10^4 C_{SCN}/C_X$		$10^3 C_{SCN}/M$	$10^3 C_X/M$	k_{exp}/s^{-1}
Constant ratios $[SCN^-]/[X^-]$				
<u>X=Cl</u>	0.48	0.05	950	0.26 ± 0.02
	5.0	0.05	100	0.20 ± 0.02
	5.0	0.15	300	0.50 ± 0.05
	5.0	0.25	500	1.0 ± 0.1
	5.0	0.475	450	1.9 ± 0.3
	10.0	0.10	100	0.40 ± 0.03
	10.0	0.30	300	1.0 ± 0.2
	10.0	0.50	500	1.6 ± 0.2
	10.0	0.95	950	3.1 ± 0.3
<u>X=Br</u>	0.5	0.045	900	1.8 ± 0.2
	1.0	0.05	500	1.5 ± 0.2
	1.0	0.09	900	2.7 ± 0.2
	2.0	0.06	300	1.2 ± 0.1
	2.0	0.10	500	2.0 ± 0.2
	2.0	0.18	900	3.7 ± 0.3
	5.0	0.05	100	0.9 ± 0.1
	5.0	0.15	300	2.2 ± 0.2
	5.0	0.25	500	4.0 ± 0.5
	5.0	0.45	900	7.0 ± 1
	10	0.10	100	1.2 ± 0.3
	10	0.30	300	3.7 ± 0.5
	10	0.50	500	5.8 ± 0.5
	10	0.90	900	11 ± 1
	50	0.50	100	4.2 ± 0.5
	50	1.5	300	12.5 ± 0.5
	50	2.5	500	20 ± 1
	50	4.5	900	35 ± 3
	100	1.0	100	7.0 ± 1
	100	3.0	300	20 ± 2
	100	5.0	500	30 ± 3

$10^4 \frac{C_{SCN}}{C_X}$	$10^3 \frac{C_{SCN}}{M}$	$10^3 \frac{C_X}{M}$	k_{exp}/s^{-1}
500	1.5	30	5.2 ± 0.5
500	2.5	50	9 ± 1
500	5.0	100	18 ± 1
1000	1.0	10	2.9 ± 0.3
1000	3.0	30	9 ± 1
1000	5.0	50	14 ± 2
1000	10	100	25 ± 3
$\bar{n}_{SCN} = 4$			
<u>X=Cl</u> 100	1.0	100	2.7 ± 0.1
100	2.0	200	4.8 ± 0.2
100	3.0	300	7.5 ± 1.0
<u>X=Br</u> $> 1 \times 10^4$	0.5	0.5	1.3 ± 0.2
	1.0	0.5	2.1 ± 0.2
	2.0	0.5	4.7 ± 0.3
	3.0	0.5	7.2 ± 0.5

Table 4. Rate constants at 25 °C, 1.00 M perchlorate medium
 m denotes a statistical factor (the number of equivalent leaving ligands in the substitution reactions).

Reaction	Rate Constant $\underline{k}/M^{-1}s^{-1}$	$(\underline{k}/\underline{m})/M^{-1}s^{-1}$
<u>Substitution</u>		
$AuCl_4^- + SCN^- \rightarrow AuCl_3SCN^- + Cl^-$	$\underline{k}_{0SCN}^{Cl} \sim 1.3 \times 10^4 \underline{a}$	0.3×10^4
$AuBr_4^- + SCN^- \rightarrow AuBr_3SCN^- + Br^-$	$\underline{k}_{0SCN}^{Br} (8.7 \pm 0.4) \times 10^4$	2.2×10^4
$\underline{t}\text{-}AuBr_2(SCN)_2^- + SCN^- \rightarrow AuBr(SCN)_3^- + Br^-$	$\underline{k}_{2tSCN} (1.2 \pm 0.2) \times 10^4$	0.6×10^4
$AuBr_3SCN^- + Br^- \rightarrow AuBr_4^- + SCN^-$	$\underline{k}_{0Br}^{Br} 14 \pm 1$	14
<u>Reduction</u>		
$AuBr_4^- + SCN^- \rightarrow AuBr_2^- + Br^- + (BrSCN)$	$\underline{k}_{r0}$	$(5 \pm 1) \times 10^4$ -
$Au(SCN)_4^- + SCN^- \rightarrow Au(SCN)_2^- + SCN^- + (SCN)_2$	$\underline{k}_{r4}$	$(2.4 \pm 0.2) \times 10^3$ -

a The value of this rate constant might be influenced by the subsequent reaction between trans- $AuCl_2(SCN)_2^-$ and SCN^- .

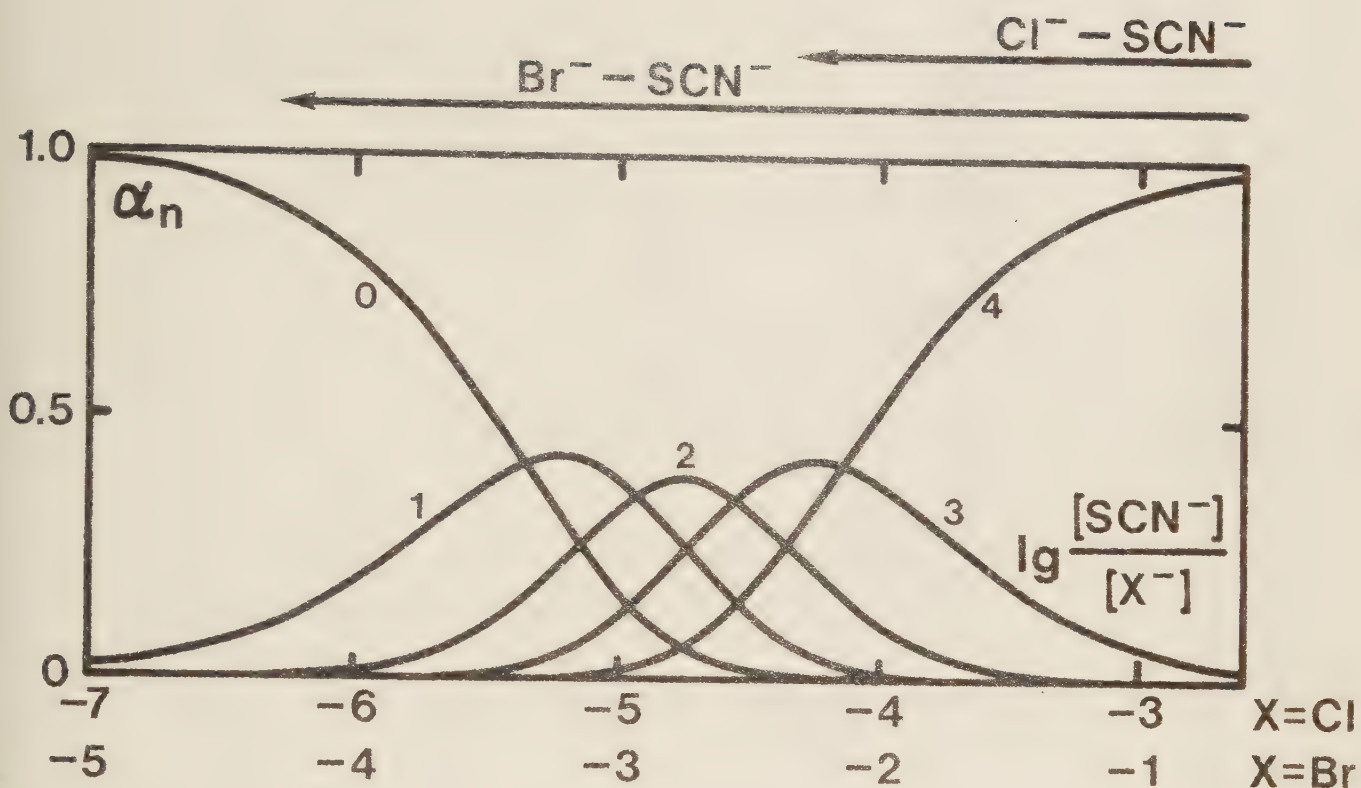


Figure 1. The distribution of gold between the species $\text{AuX}_{4-\underline{n}}(\text{SCN})_{\underline{n}}^-$ $\underline{n}=0,1,2,3,4$; $\text{X}=\text{Cl},\text{Br}$, calculated from the β_4 values in Ref. 12 and assuming a statistical distribution of the gold. The arrows denote experimentally accessible regions.

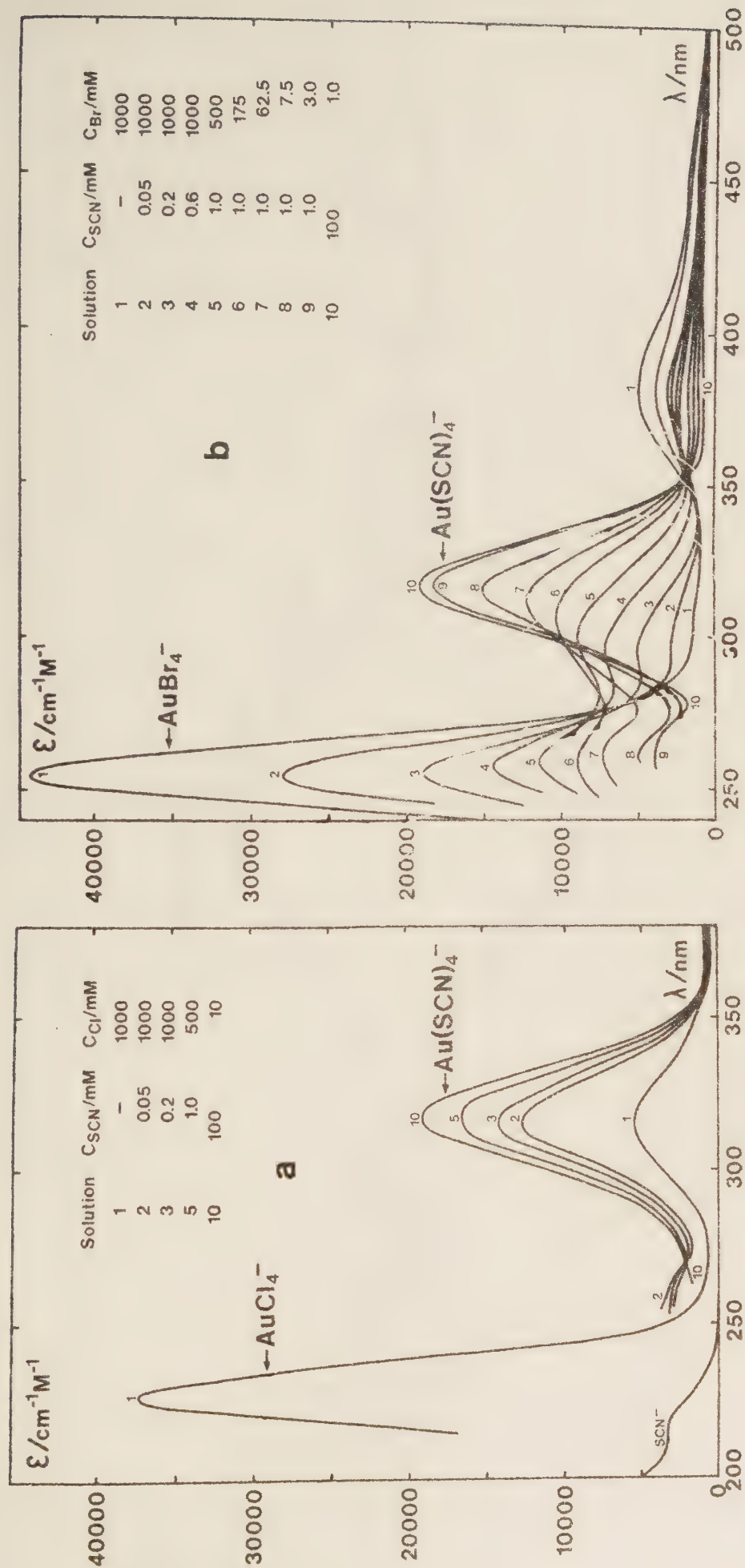


Figure 2. Flow spectra of solutions containing equilibrium mixtures of the thermodynamically unstable complexes $AuX_{4-\bar{n}}(SCN)_{\bar{n}}^-$, $\bar{n}=0, 1, 2, 3, 4$; $X=Cl$ (a), $X=Br$ (b).

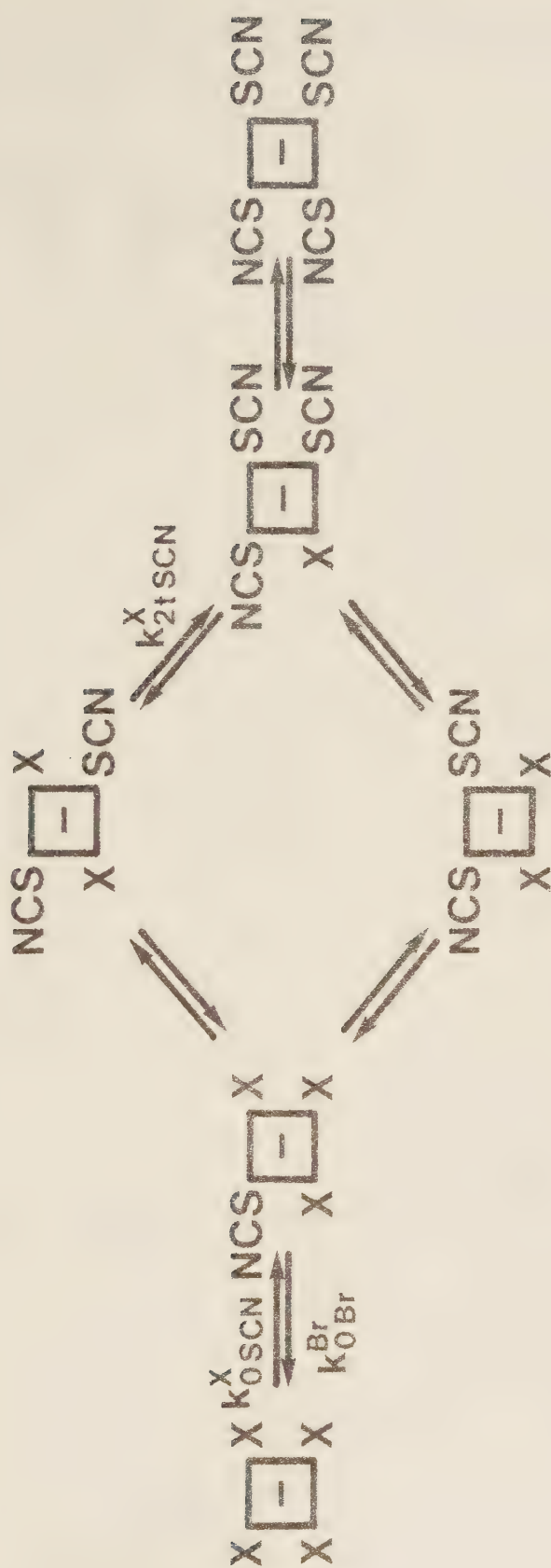


Figure 3. Reaction model for the substitutions. The reaction via

the cis-isomer is negligible because of the large

difference in trans-effect between X^- and SCN^- .

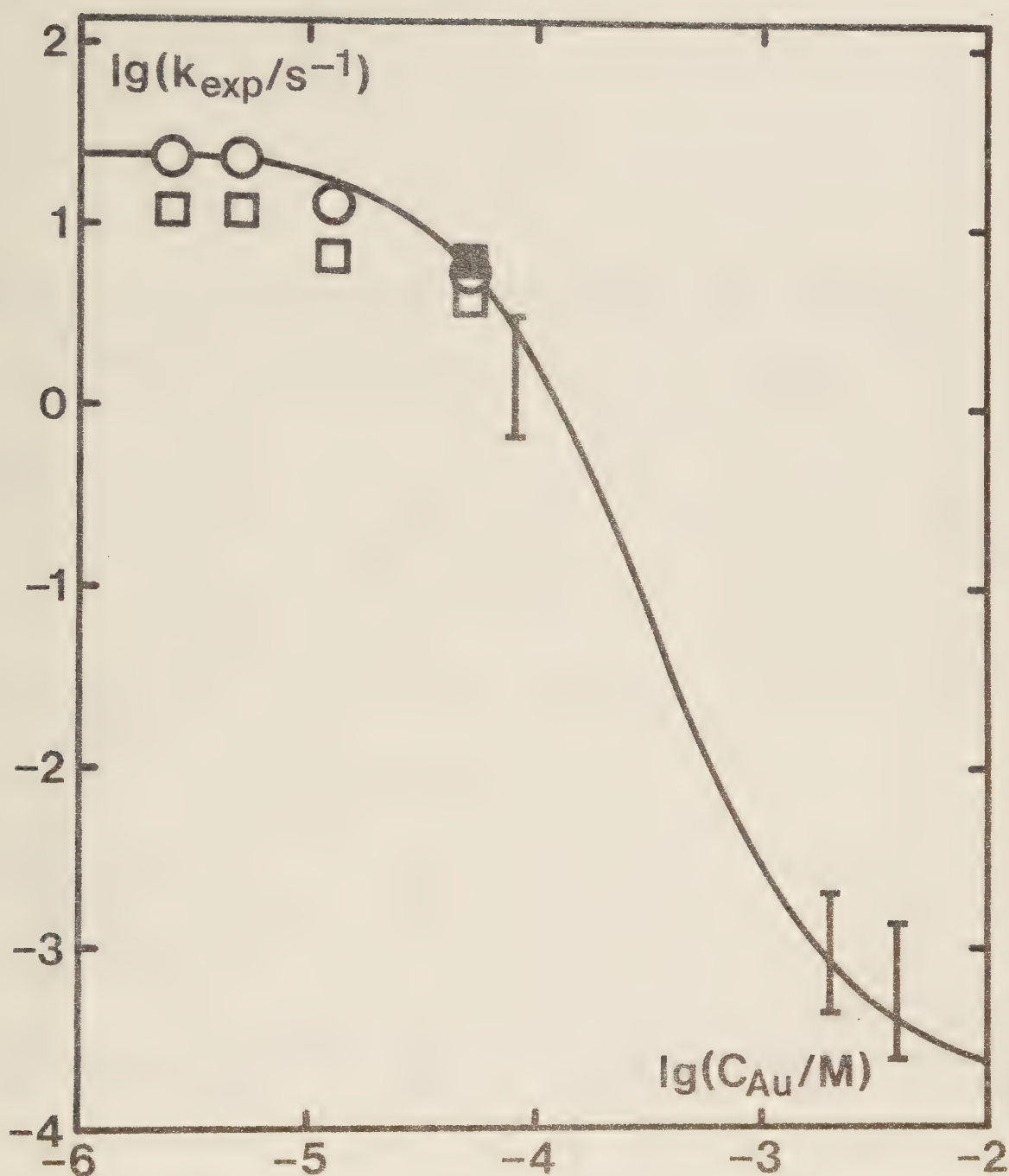


Figure 4. The observed rate constant for the reduction as a function of C_{Au} in a logarithmic scale.

$C_{Au}=2.5 \times 10^{-6}$ M, 5×10^{-6} M, 1.25×10^{-5} M and 5×10^{-5} M with $C_{SCN}=0.100$ M, (○), or 0.01 M, (□), $C_{Cl}=0.100$ M and $C_{H^+}=10$ mM. The value from ref. 7 with $C_{Au}=4 \times 10^{-5}$ M, $C_{SCN}=10$ mM, $C_{Cl}=0.100$ M and $C_{H^+}=2$ mM (■) and estimated values from ref. 6 with $C_{Pt} \approx 8 \times 10^{-5}$ M and $C_{SCN}=10$ mM and from ref. 1 with $C_{Pt} 2 \times 10^{-3}$ M and 4×10^{-3} M, $C_{SCN} \sim 100$ mM are also included in the Figure.

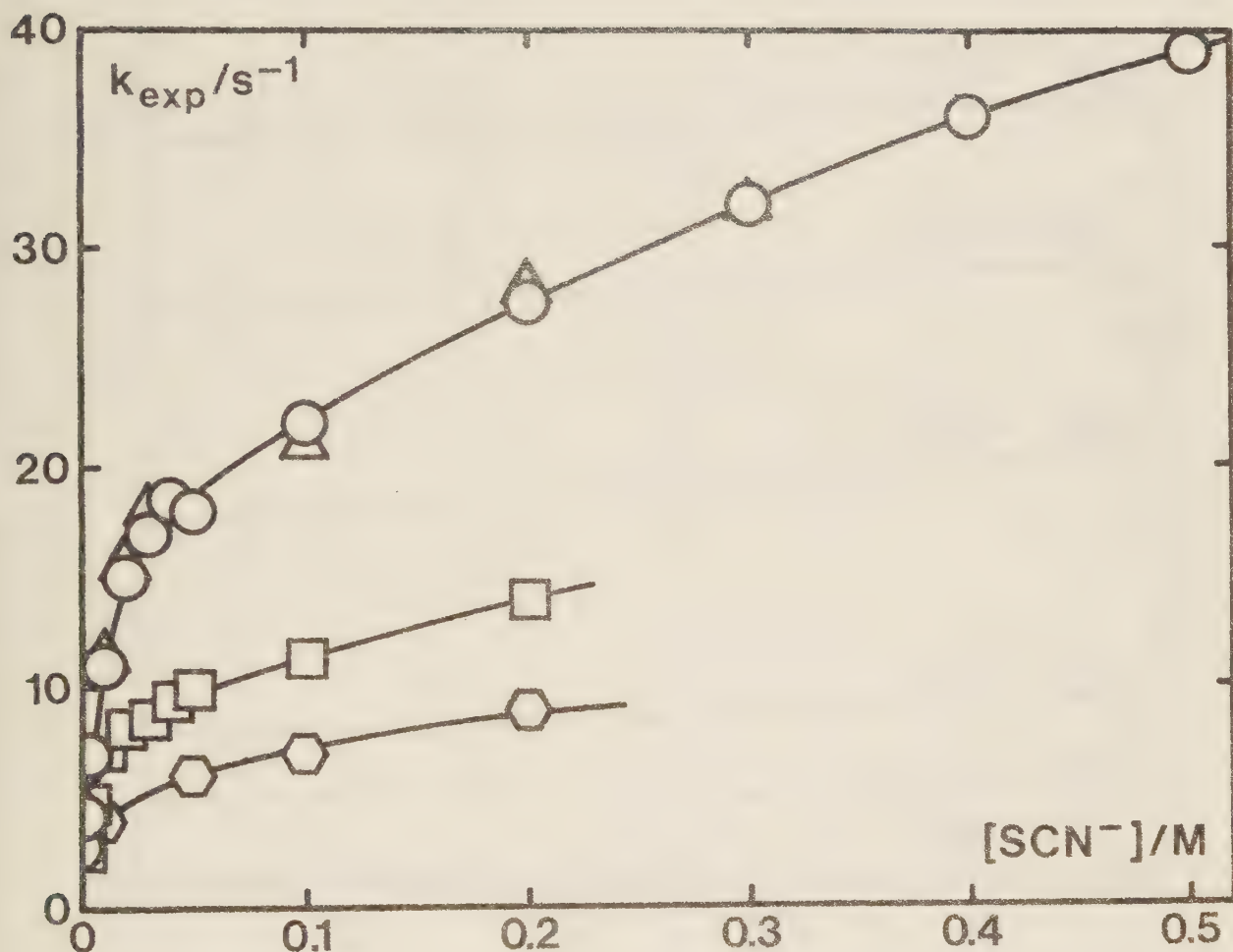


Figure 5. The observed rate constant for the reduction of AuCl_4^- vs. the thiocyanate concentration for large concentrations of thiocyanate. $\underline{C}_{\text{Cl}} = 0.100 \text{ M}$, $\underline{C}_{\text{Au}} = 2.5 \times 10^{-6} \text{ M}$ (Δ), $5 \times 10^{-6} \text{ M}$ ($\bigcirc$), $1.25 \times 10^{-5} \text{ M}$ ($\square$) and $5 \times 10^{-5} \text{ M}$ ($\bigcirc$).

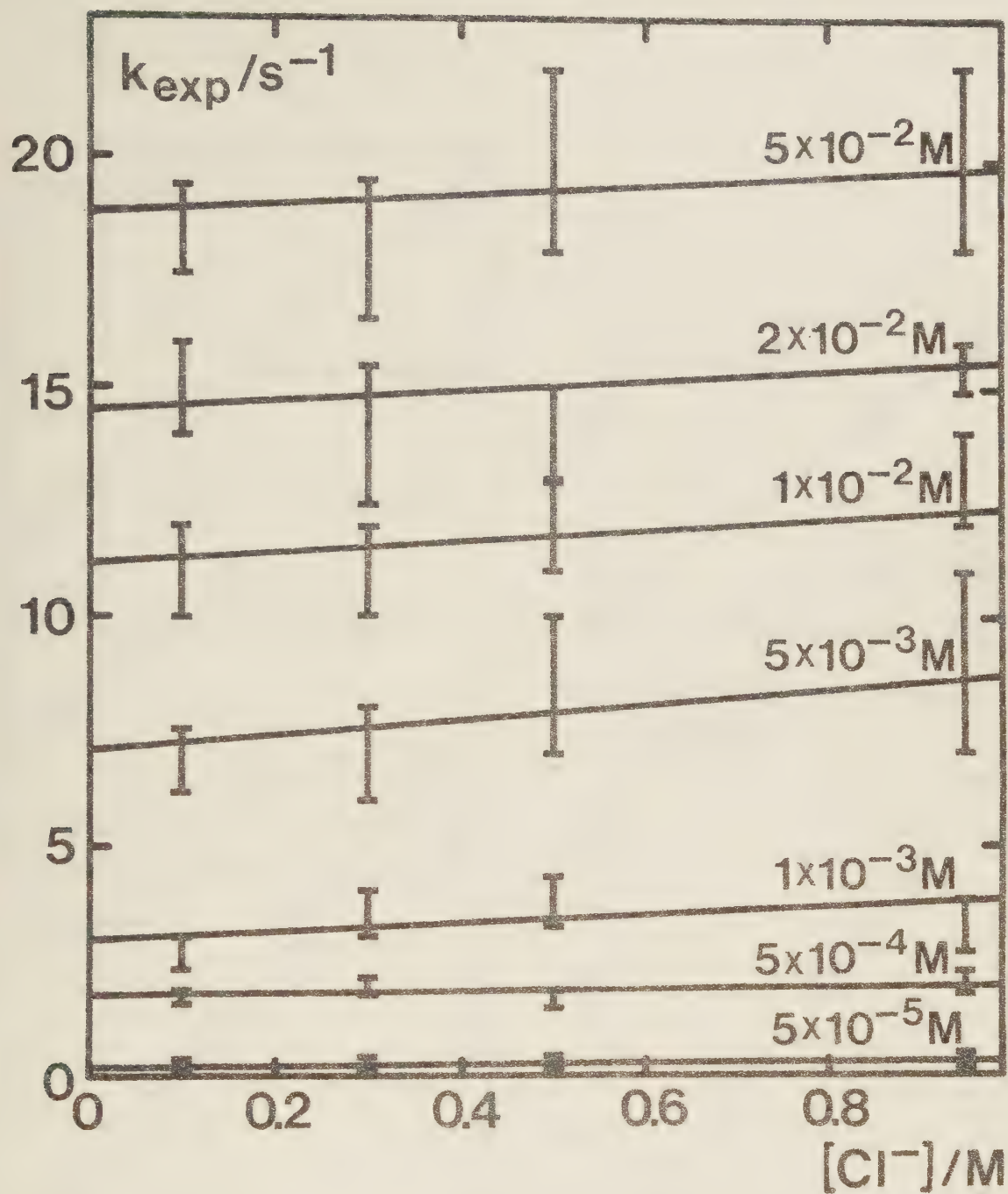


Figure 6. The observed rate constant for the reduction of AuCl_4^- by thiocyanate as a function of the chloride concentration for various thiocyanate concentrations.

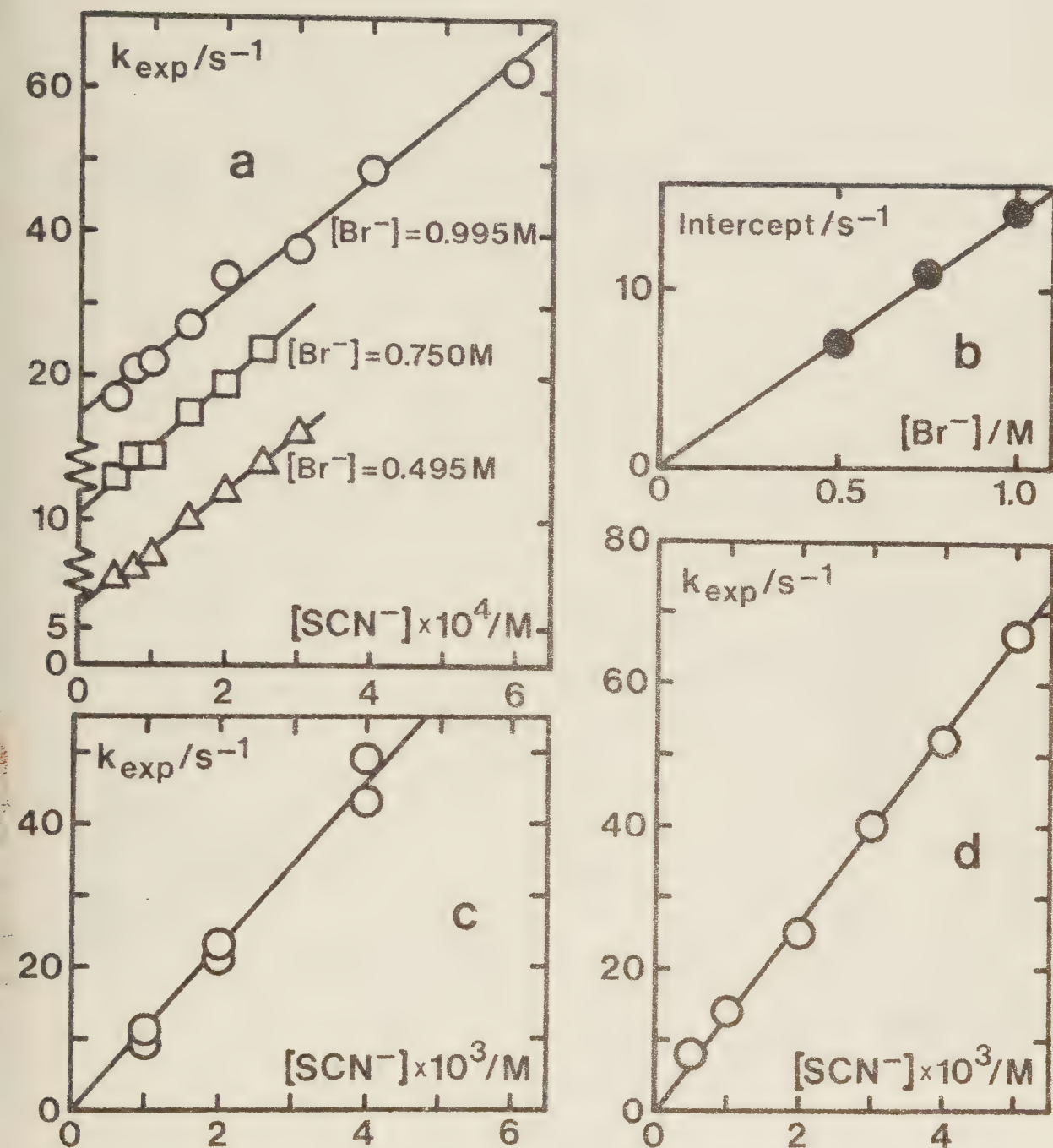


Figure 7. Plots of the observed rate constants vs. the concentration of thiocyanate for the substitution reactions (8)-a, (9)-(c) and (10)-d. In (b), the intercepts from Fig. 7a have been plotted vs. $[\text{Br}^-]$.

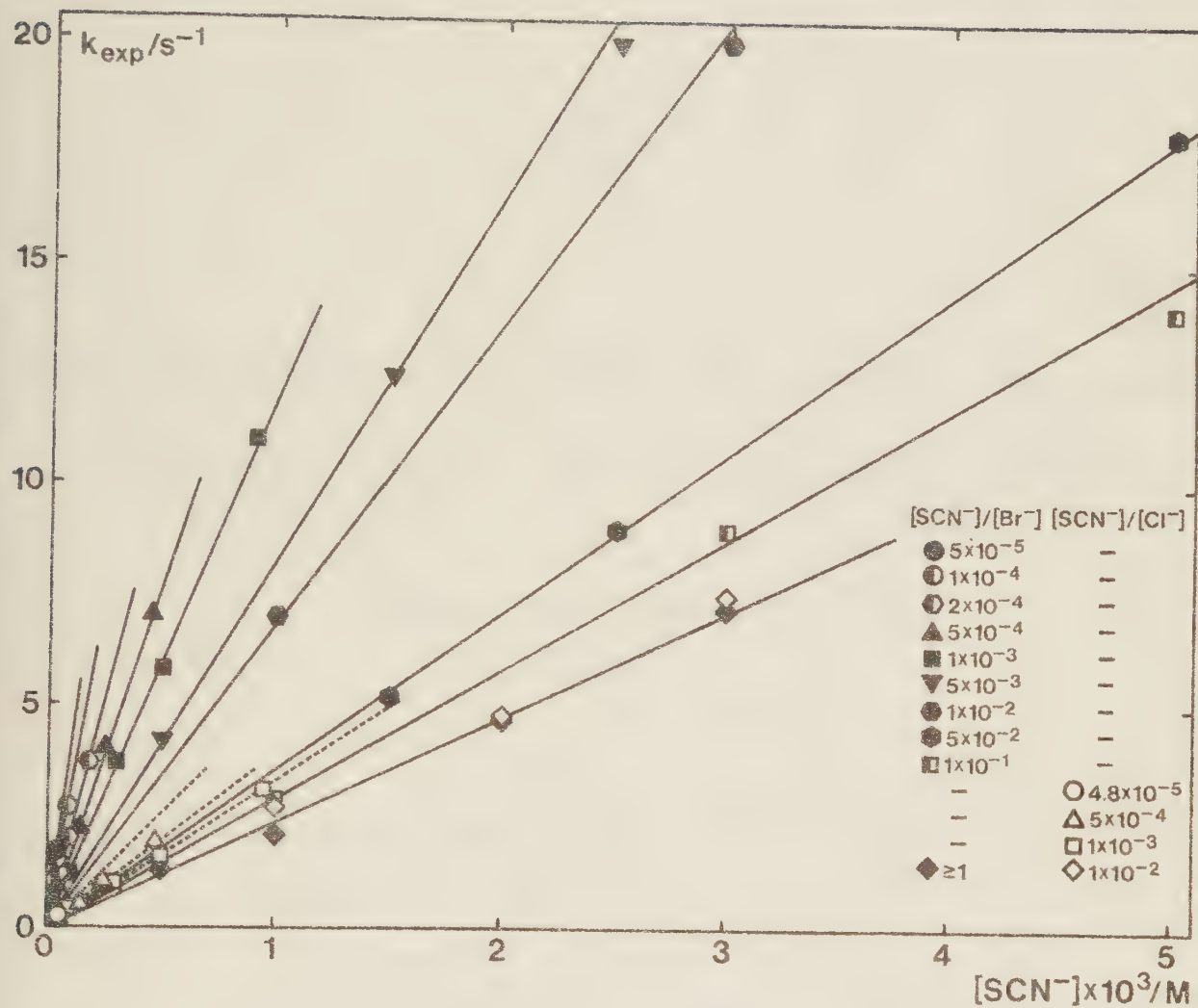


Figure 8. The observed rate constant for the reduction of Au(III) by thiocyanate as a function of the thiocyanate concentration at constant ratios $[\text{SCN}^-]/[\text{X}^-]$.

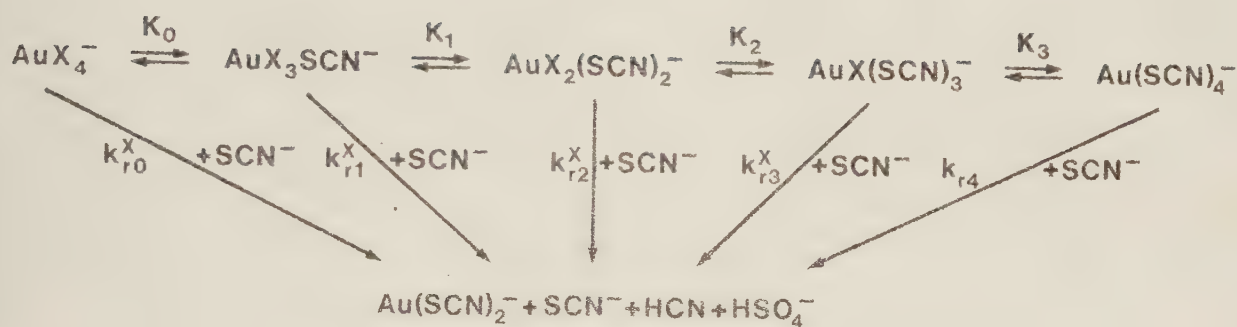
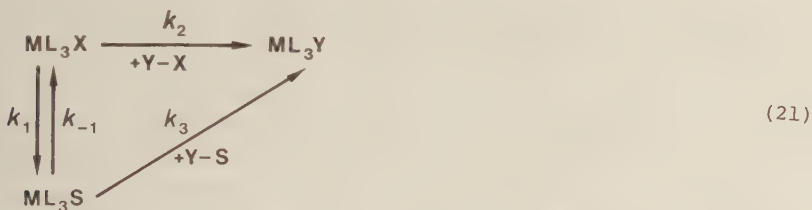


Figure 9. Reaction model for the redox reaction. K_n , $n=0,1,2,3$ denote the stepwise equilibrium constants for the processes (5). k_r^X , $n=0,1,2,3,4$ and $X=\text{Cl}, \text{Br}$ denote the reduction rate constants for the various complexes $\text{AuX}_{4-n}(\text{SCN})_n^-$.

$$k_{\text{exp}} = k_{\text{nCl}}[\text{Cl}^-] + k_{\text{nBr}}[\text{Br}^-] \quad (20)$$

For the reactions studied in papers I and II (cf. Table II) reverse processes were suppressed by large concentrations of entering ligand. The general scheme (14) is then reduced to scheme (21), which is valid for all these experiments except that between *trans*-PtCl₂(H₂O)₂ and ethene (*vide infra*). Reversible solvolysis is considered. (See also III).



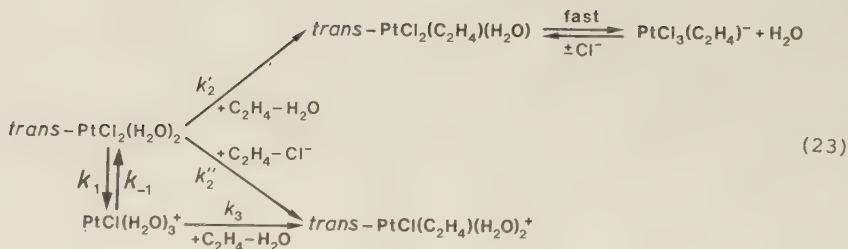
If the intermediate solvento complex ML₃S is present in steady-state concentrations, the pseudo first-order rate constant for excess entering ligand is described by

$$k_{\text{exp}} = \frac{k_1}{1 + k_{-1}[\text{X}]/k_3[\text{Y}]} + k_2[\text{Y}] \quad (22)$$

For $k_{-1}[\text{X}] \ll k_3[\text{Y}]$ eqn. (22) transforms to the usual simple eqn. (2).

Those reactions in paper I, where the reverse reactions are negligible, also conform to scheme (21). For these reactions, for example $\text{PtCl}_4^{2-} + \text{Br}^- \rightarrow \text{PtCl}_3\text{Br}^{2-} + \text{Cl}^-$ the solvent path is predominant (cf. page 24).

In the reaction between *trans*-PtCl₂(H₂O)₂ and ethene (III), product analysis shows that both a chloride ligand and a water ligand are substituted in two parallel paths. A detailed mechanism for the reaction is described by (23).



Steady-state conditions for $\text{PtCl}(\text{H}_2\text{O})_3^+$ give the observed pseudo first-order rate constant for excess ethene

$$k_{\text{exp}} = \frac{k_1}{1 + k_{-1}[\text{Cl}^-]/k_3[\text{C}_2\text{H}_4]} + (k_2' + k_2'')[\text{C}_2\text{H}_4] \quad (24)$$

The first term corresponds to the first one in eqn. (22). The value of k_1 calculated from the small intercept of the k_{exp} vs. $[\text{C}_2\text{H}_4]$ plot according to eqn. (24) agrees within the experimental errors with the rate constant for the acid hydrolysis of $\text{trans-PtCl}_2(\text{H}_2\text{O})_2$. Analysis of the product shows that the ratio k_2'/k_2'' is 1.5 ± 0.2 (cf. III).

For the corresponding reaction between $\text{trans-PtCl}_2(\text{H}_2\text{O})_2$ and DMSO (as well as with bromide, iodide and thiocyanate) the k_2' -path disappears and only the k_2'' and the k_1 -path can be observed (II).

Several studies on the solvent path have appeared in the literature recently²³⁻³⁵ Most reactions are reported to proceed *via* the usual two-term rate expression (2), for example the tetrachloroplatinate(II)-ethene-reaction studied by Green and Wilson.³⁵ Sometimes, however, reactions have been reported to proceed exclusively *via* a direct reaction between the substrate complex and the entering ligand with no contribution from a path involving solvolysis of the substrate complex.^{28,30-32} For instance, Mureinik³¹ has reported that thiocyanate does not react with aqua complexes of platinum(II), *vs.* $\text{PtCl}_3\text{H}_2\text{O}^-$, whereas its reaction with PtCl_4^{2-} was normal. The experiments in paper II definitely disprove Mureinik's conclusion and show that there is nothing "anomalous" with thiocyanate in this respect.

A critical examination of other literature data also shows that the proposed deviations from the two-term rate expressions as a rule derive from the experimental conditions used and the chemical properties of the particular system. In some cases, the substrate complex reacts considerably faster with the entering ligand Y than with the solvent, that is $k_1 \ll k_2[Y]$. An example is given by the gold(III) complexes in the present study (IV).

There is another possibility for the disappearance of the solvent path which is not so obvious. It appears from the schemes (14), (21) and (23) that the leaving group, X, competes with the entering group, Y, for the aqua complexes in the reactions studied. If no extra leaving ligand is added, i.e. $k_{-1}[X] \ll k_3[Y]$, eqns. (22) and (24) transform to the usual expression (2). The observed appearance or non-appearance of a k_1 -term will thus depend on the relative values of the terms $k_{-1}[X]$ and $k_3[Y]$. By increasing the concentration of the leaving ligand the first term in eqns. (15), (22) and (24) will decrease and might become negligibly small compared to the second term in these equations. Examples of such behaviour are the reactions between PtCl_4^{2-} and olefins studied by Milburn and Venanzi³⁰ and between PdCl_4^{2-} and various substituted thioureas, studied by Bekker and Robb.^{28,32} The experimental design was similar in all these studies in that the leaving ligand was present in a large excess, and that the solvent path therefore was effectively quenched. As discussed comprehensively in III, none of these studies give any support for the assumptions by these authors that Y reacts slowly with the solvento intermediate, i.e. $k_2 \sim k_3$ or $k_2 > k_3$.

The simplest experimental design is to perform the experiments using constant ratios $[X]/[Y]$. Linear plots of k_{exp} vs. the concentration of entering ligand will then result. The present study gives several examples. The reaction between PtCl_4^{2-} and iodide, DMSO and ethene and the reaction between $\text{trans-PtCl}_2(\text{H}_2\text{O})_2$ and ethene were followed using constant ratios $[\text{Cl}^-]/[\text{DMSO}] = 10$, $[\text{Cl}^-]/[\text{I}^-] = 200$, $[\text{Cl}^-]/[\text{C}_2\text{H}_4] = 100$ and $[\text{Cl}^-]/[\text{C}_2\text{H}_4] = 10$, respectively. The intercepts of the linear plots of k_{exp} vs. $[Y]$ are then given by the term $k_1/(1+k_{-1}[X]/k_3[Y])$, cf. eqns. (22) and (24), and as the quotient $[X]/[Y]$ is constant and the rate constants k_{-1} and k_3 are known in all cases (see Table II) the acid

hydrolysis rate constant k_1 , can be calculated from these intercepts.

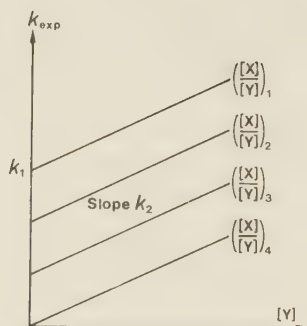


Figure 4. Graphical representation of eqn (22) for various constant ratios $[X]/[Y]$.

Figure 4 shows a graphical representation of eqn. (22) for various constant ratios $[X]/[Y]$, the limiting values of the intercepts being 0 for $k_{-1}[X] \gg k_3[Y]$ and k_1 for $k_{-1}[X] \ll k_3[Y]$. A plot of the inverse intercepts vs. $[X]/[Y]$ gives linear plots according to eqn. (25).

$$(\text{intercept})^{-1} = 1/k_{-1} + (k_{-1}/k_1 k_3) \cdot ([X]/[Y]) \quad (25)$$

which is analogous to eqn. (5) in de Waal's and Robb's recent paper.³³ If the condition $[X]/[Y] = \text{constant}$ is not fulfilled, curved plots of k_{exp} vs. $[X]$ or k_{exp} vs. $[Y]$ will be obtained (cf. Ref. 34).

In a recent study of the reactions between $\text{Pt}(\text{terpy})\text{Cl}^+$ and various nucleophiles, Mureinik and Bidani²³ reported a solvent path of the form $1/(a[\text{Cl}^-] + b)$, a and b being constants and chloride the leaving ligand. This dependence is in accord with

the mechanism (21) and the rate law (22) for constant concentrations of entering ligand. Thus, the experiments give no evidence for any "unusual" behaviour of the solvent path, and there seems to be no justification for the alternative mechanism suggested by these authors.

To conclude, the present experimental information gives no reasons to expect any mechanistic deviations from the general schemes (14) (general formulation in scheme (1) of III) and (21).

5.2. Empirical description of reactivity

5.2.1. *The charge of the complex*

It is reasonable that the ionic charge of the complexes should influence the rate of reaction especially for charged entering ligands, c_f . Elding.⁷¹ For instance, the rate constant for the entering ligand bromide is larger than that for DMSO when the substrate is $\text{PtCl}(\text{H}_2\text{O})_3^+$, whereas the reverse is true for PtCl_4^{2-} as substrate complex (II). It is difficult to separate the influence of the ionic charge of the complex from, for instance, the *cis*-effect. In spite of this a charge factor q for the different entering groups for the substrate complexes $\text{PtCl}_n(\text{H}_2\text{O})^{2-n}$, $n=0,1,2,3,4$ can be calculated. The procedure is described in paper II. The rate constants for substitution of water by entering nucleophiles are described by the empirical equation (4) given on page 9. By assuming a charge factor q of approximately 5 for chloride and bromide as entering ligands (c_f , ref. 71), q for iodide and thiocyanate was determined to 5 ± 1 (II), for DMSO to 0.35 ± 0.1 (II) and for C_2H_4 to 1.0 ± 0.2 (III).

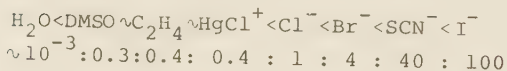
DMSO is a polar molecule with a charge of about +0.5 at the sulfur atom.⁵⁶ The charge factors for DMSO and ethene imply that DMSO behaves as a positively charged entering group (compare also 5.2.2.) whereas ethene behaves like a neutral group.

In papers I and IV, where both complexes and ligands have constant ionic charges in the reactions compared, no relative charge effects should be expected.

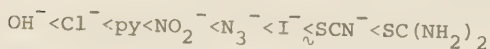
5.2.2. The entering group

One of the main features of an associative process is a strong dependence of rate on the nature of the entering group. It appears from Table II that the reaction rate is increased more than three orders of magnitude from the slowest (DMSO) to the fastest (I^-) entering ligand in the reactions with the six aqua complexes studied. Water can also be included in this comparison. If the acid hydrolysis rate constants of $PtCl_4^{2-}$ and $trans-PtCl_2(H_2O)_2$ are expressed as second-order constants by division with $[H_2O]=55\text{ M}$ (see Table II) it turns out that water is a very bad entering ligand about 10^2 - 10^3 times less efficient than DMSO and C_2H_4 . Studies of the k_1 -path for the reaction of $trans-Pt(py)_2Cl_2$ (py =pyridine) with labeled chloride in various solvents⁷² have also shown that DMSO is a better entering group than water.

Hence, the average entering-group reactivity order is (cf. ref. 39. The value for $HgCl^+$ from ref. 82)



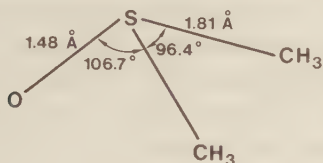
A similar sequence of reactivity was obtained for the reaction between $Pt(dien)Br^+$ and various entering groups:⁷³



and other studies⁷⁴ have also given approximately the same orders for entering-ligand efficiency. The difference between the efficiencies of iodide and thiocyanate as entering ligands is not large. Sometimes, thiocyanate is a better entering group than iodide and sometimes the reverse is valid, compare the two series above.

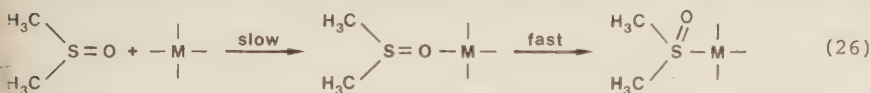
Langford and Gray⁸ point out the striking resemblance of the average ligand reactivity order and the *trans*-effect order and suggest that a good *trans* labilizer is also a good entering group in square-planar substitutions. The present results show that such a generalisation is not always true. Both DMSO and C_2H_4 are bad entering groups in spite of their very large *trans*-effects, compare the *trans*-effect order on page 34.

The low efficacy of DMSO as entering ligand might be due to steric hindrance. Ligands coordinating *via* the sulfur atom are generally good entering groups, at least when the sulfur atom is readily accessible, as for instance in linear thiocyanate, and in thiourea, ($\text{S}=\text{C}(\text{NH}_2)_2$). DMSO, on the other hand, has a pyramidal structure with the sulfur atom at the top (see ref. 56),



which makes the sulfur less accessible.

A description of the reaction with DMSO in terms of a rate-determining step to an oxygen coordinated complex followed by a fast rearrangement to the thermodynamically stable sulfur bonded product according to (26) seems less probable,



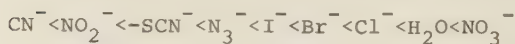
since the oxygen atom in DMSO is negatively charged, and we have found (cf. Table II) that DMSO behaves like a positively charged entering ligand, being a better entering group for negatively charged substrates. This speaks in favour of an attack *via* the positively charged sulfur atom.

The low efficacy of ethene as entering ligand is probably also due to the specific steric requirements needed for the formation of the transition state from the olefin and the substrate complex.

5.2.3. The leaving group

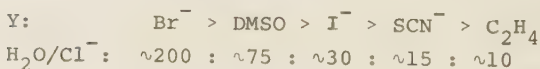
Another factor that affects the reaction rate is the nature of the leaving group. Generally, the stronger the metal-ligand bond the slower is the replacement of the leaving group and it is interesting that leaving groups of large trans-effect are replaced very slowly.

The following average leaving group order has been obtained for the reaction between $\text{Pt}(\text{dien})\text{X}^+$ and pyridine:⁷⁴



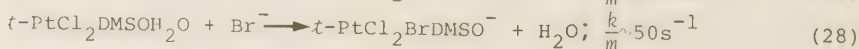
Water is usually considered to be an excellent leaving ligand.⁷⁷ However, when comparing different leaving groups due consideration must always be taken to the effect of the *trans*-ligand. For example, in the reactions between *trans*- $\text{PtCl}_2(\text{H}_2\text{O})_2$ and Cl^- , Br^- , I^- , SCN^- and $\text{DMSO}(\text{II})$, the chloride ligand and not the water ligand is substituted, obviously because the *trans*-effect of chloride is so large (300:1) compared to water (cf. section 5.2.4.). Water ligands *trans* to each other are thus replaced very slowly.⁷⁸

In an associative mechanism, the kinetic properties of the leaving group should be expected to depend on the nature of the entering nucleophile and the *trans*-ligand: Comparisons of the rate constants $k/(\text{mol}^2\text{s}^{-1})$ in Table II for e.g. reactions (4) and (2), (3a) and (5), (3b) and (4) and (2) and (3b) show that water is a more efficient leaving ligand than chloride but the relative efficacy $\text{H}_2\text{O}/\text{Cl}^-$ as leaving ligands changes with the nature of the entering ligand Y in the following manner:

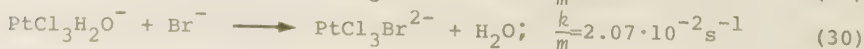
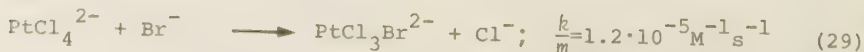


There is no obvious relationship between the ordering of ligands in this series and for instance *trans*-effects (cf. page 34) or entering-ligand effects (cf. page 30).

Comparisons between the two pairs of reactions (from Ref. 79 and paper I, respectively).



and



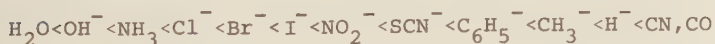
give the relative efficacy $\text{H}_2\text{O}/\text{Cl}^-$ as leaving ligands equal to 2×10^2 for DMSO as *trans*-ligand and 2×10^3 for Cl^- as *trans*-ligand. Thus the relative efficacy of leaving ligands depends on the nature of the *trans*-ligand.

It appears from comparisons between reactions Q and W and U and X in Table I for $\text{M}=\text{Pt}$ that there is no significant difference between chloride and bromide as leaving groups for constant *trans*- and entering ligands. Similar results are obtained by Cattalini et al.^{11,80} Elding³⁹ has found that bromide is about three times better as leaving ligand than chloride. Water is between 200 and 800 times better as leaving group than the two halides (I). Furthermore, the influence of the leaving group appears to be of similar magnitude for gold(III) and platinum(II) complexes (IV).

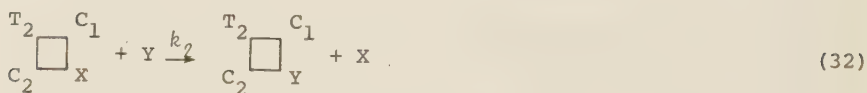
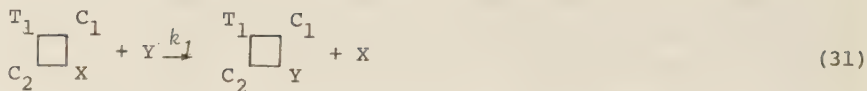
5.2.4. The *trans*-ligand

In the present terminology⁷⁵, the concept *trans*-effect will be used to describe kinetic properties of the substrate complex. The *trans*-effects are thus obtained from comparisons of rate constants and are related to energy differences between transition states and ground states. The term *trans*-influence, on the other hand, will refer to thermodynamic properties, bond lengths etc. The *trans*-influence is related to energy differences between complexes in their ground states, and may be obtained, for instance, from comparisons of equilibrium constants.

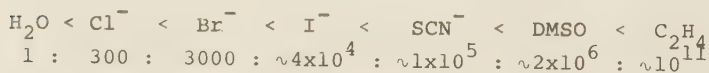
5.2.4.1. *Trans*-effect. The *trans*-effect was first recognized in preparative chemistry. It was found that some ligands had a stronger tendency than others to direct an incoming group to the position *trans* to itself. In platinum(II) complexes this ability decreases approximately in the following order:⁸¹



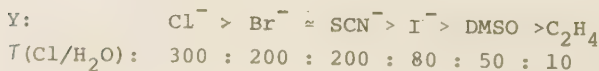
In the present work, the relative *trans*-effect has been defined as the quotient k_1/k_2 between the rate constants for the elementary reactions (31) and (32)



after a correction for the influence of the ionic charge of the complexes has been made. Using such comparisons of rate constants, Elding and Ö. Gröning⁷⁵ have quantitatively evaluated the *trans*-effect of DMSO relative to H₂O, Cl⁻ and Br⁻ in the platinum(II) complexes for water as entering nucleophile. The *trans*-effects of SCN⁻ and I⁻ have also been determined.³⁹ The following *trans*-effect order for platinum(II) was obtained:

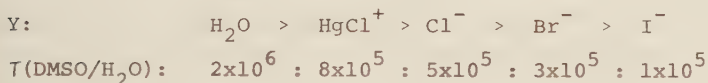


The relative *trans*-effect Br⁻/Cl⁻ determined from the rate constants for the reactions of chloro-bromo complexes of platinum(II) (paper I), depends on the nature of the entering group. The value is 10_{±2} for water as entering ligand (comparisons of for example reactions R,Q; U,S and X,S in Table I) and 6_{±2} for halide as entering ligand (comparisons of e.g. reactions A,B; F,D and L,J in Table I). Similar comparisons for the gold(III) complexes show that the relative *trans*-effect Br⁻/Cl⁻ is 14_{±3} (IV). The relative *trans*-effect Cl⁻/H₂O (I,II) is also found to be dependent on the nature of the entering group. After correction for the ionic charges of the complexes, the relative *trans*-effect Cl⁻/H₂O can be calculated from e.g. reactions (2), (6); (4), (6) and (5), (6) in Table II and the following values are obtained for different ligands T:

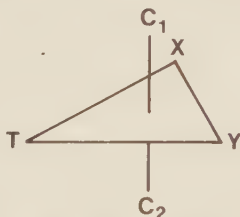


Thus, the *trans*-effect of Cl⁻ relative to H₂O decreases when the *trans*-effect of the entering group increases. Bearing in mind the

large difference in rate constant (about 10^4) for different entering groups (see Table II and p. 30) the increase by a factor of about 30 for the relative *trans*-effect $\text{Cl}^-/\text{H}_2\text{O}$ for different entering groups is a rather small effect. Similar results have been obtained by Elding and Gröning⁸² in the study of the relative *trans*-effect $\text{DMSO}/\text{H}_2\text{O}$ in the complexes $\text{PtDMSO}(\text{H}_2\text{O})_3^{2+}$ and $\text{Pt}(\text{H}_2\text{O})_4^{2+}$ with the entering groups HgCl^+ , Cl^- , Br^- and I^- . The rate constants for the different entering ligands differ by as much as a factor of 10^6 (the entering ligand order is $\text{H}_2\text{O} < \text{HgCl}^+ < \text{Cl}^- < \text{Br}^- < \text{I}^-$, compare page 30), while the relative *trans*-effect $\text{DMSO}/\text{H}_2\text{O}$ is changed by a factor of about 10 for the different entering ligands (the value for $\text{Y}=\text{H}_2\text{O}$ from the series on page 34):



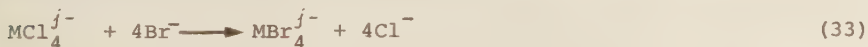
The relative *trans*-effect depends on the nature of the entering ligand Y. This is consistent with an associative mechanism *via* a trigonal-bipyramidal intermediate



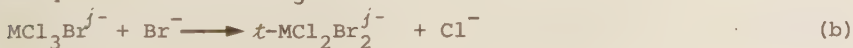
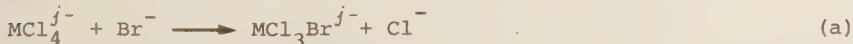
where the *trans*-ligand, the leaving ligand and the entering ligand interact in the trigonal plane around the platinum atom.

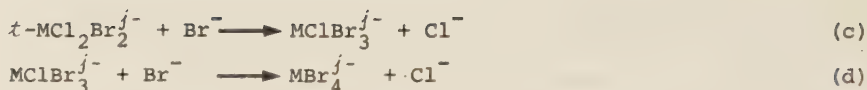
The great importance of the *trans*-effect for the over-all kinetics in some of the studied systems, involving series of stepwise substitutions, can be illustrated by the following examples:

The over-all reaction ($\text{M}=\text{Au}, \text{Pt}; j=1,2$)



occurs *via* the consecutive steps (a) to (d)





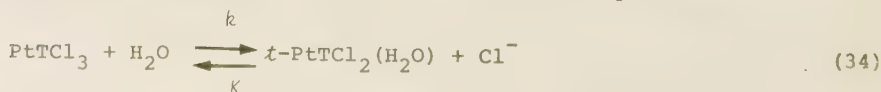
The reaction *via* the *cis*-isomer will account for only about 10% of the overall reaction and can be neglected (see Table I). The reaction scheme for the overall process is shown in Figure 1.

Cattalini and co-workers⁴¹ have proposed that the rate-determining steps for the conversion of MCl_4^{j-} to MBr_4^{j-} , $\text{M}=\text{Pt}, \text{Au}$, are the reactions (a) and (c) whereas the reactions (b) and (d) were considered to be fast processes due to the "large" difference in *trans*-effect between bromide and chloride. It is true that the overall process (33) occurs mainly via the intermediate complexes $\text{MCl}_3\text{Br}^{j-}$, *trans*- $\text{MCl}_2\text{Br}_2^{j-}$ and MClBr_3^{j-} both for Pt(II) and Au(III). But in neither of the systems are the four reactions kinetically separated (see Table I).

In the substitution reactions of halide by thiocyanate discussed in V, however, the model proposed by Cattalini is valid, since the difference in *trans*-effect between SCN^- and Cl^- or Br^- is sufficiently large (the relative *trans*-effect SCN^-/X^- is about 300 for $\text{X}=\text{Cl}$ and about 30 for $\text{X}=\text{Br}^-$) cf. the series on page 34.

5.2.4.2. *Trans-influence*. There are several studies of the *trans*-influence in the literature. Tobe (cf. ref 9 page 56) has discussed the variation of the length of the Pt-Cl bond for different *trans*-ligands. Unfortunately, the *cis*-ligands in all complexes studied were also varied which might influence the correlation between the *trans*-ligand and the length of the Pt-Cl bond.

The complexes PtCl_4^{2-} , PtDMSOCl_3^- and $\text{PtC}_2\text{H}_4\text{Cl}_3^-$ have all the same *cis*-ligands. The length of the Pt-Cl bond in these complexes is shown below where the statistically corrected equilibrium and rate constants of reaction (34) are also given.



where $\text{T}=\text{Cl}^-$, DMSO or C_2H_4 .

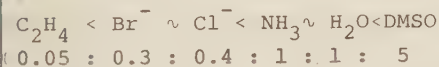
	Cl (ref.83-85)	DMSO (ref.86)	C ₂ H ₄ (ref.58)
	$\begin{array}{c} \text{Cl} \xrightarrow{2.305} \text{Pt} \xrightarrow{2.305} \text{Cl} \\ \\ 2.305(7) \\ \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{Cl} \xrightarrow{2.296(6)} \text{Pt} \xrightarrow{2.302(6)} \text{Cl} \\ \\ 2.318(5) \\ \\ \text{Cl} \end{array}$	$\begin{array}{c} \text{Cl} \xrightarrow{2.296(7)} \text{Pt} \xrightarrow{2.314(7)} \text{Cl} \\ \\ 2.327(5) \\ \\ \text{Cl} \end{array}$
$\frac{K}{m} / M^{-1}$	$3.2 \times 10^{-3} (\text{ref.87})$	$5.3 \times 10^{-3} (\text{ref.75})$	$3.5 \times 10^{-3} (\text{ref.88})$
$\frac{k}{m} / s^{-1}$	$1.0 \times 10^{-5} (\text{ref.37})$	$0.10 (\text{ref.75})$	$\sim 10^4 (\text{ref.75})$

As can be seen the *trans*-Pt-Cl bond increases slightly in the solid state for T=DMSO and C₂H₄. It appears that the equilibrium constants are nearly independent of the nature of the *trans*-ligand whereas the rate constants for the acid hydrolyses are changed by a factor of as much as 10⁹. Hence, for the ligands discussed here, the *trans*-influence plays a minor role compared to the kinetic *trans*-effect.

5.2.5. The *cis*-ligand

The *cis* groups have only a small effect on the substitution rates. The *cis*-effect is relatively more important only in the presence of a weak *trans*-ligand. In the chloro-ammine-platinum(II) complexes studied by Martin and co-workers⁸⁹, the relative *cis*-effect $\text{NH}_3/\text{Cl}^- \sim 2$ is of the same importance as the relative *trans*-effect $\text{Cl}^-/\text{NH}_3 \sim 1.5$.

A good *cis*-effect ligand is not always a bad *trans*-effect ligand. Elding and Ö. Gröning⁷⁵ have recently determined the following *cis*-effect order for platinum(II)-substrates:



DMSO has both a large *trans*-effect and a large *cis*-effect. The *cis*-effect spans only over two orders of magnitude in the studied

systems, while the *trans*-effect for the same ligands changes with as much as a factor of 10^{11} (see page 34).

The influence of the entering group on the relative *cis*-effect Cl^-/Br^- and $\text{Cl}^-/\text{H}_2\text{O}$ has been investigated in I and II, III, respectively. The relative *cis*-effect Cl^-/Br^- , calculated both for acid hydrolysis (1.4 ± 0.2) and for halide exchanges (1.6 ± 0.2), and the relative *cis*-effect $\text{Cl}^-/\text{H}_2\text{O}$ (0.5 ± 0.2) was independent of the entering ligand Y. (Y = Cl^- , Br^- , I^- , SCN^- , DMSO and C_2H_4). Moreover, the relative *cis*-effect Cl^-/Br^- for the corresponding mixed chloro-bromo complexes of Au(III) was of similar magnitude: 1.1 ± 0.1 (IV).

The insensibility of the relative *cis*-effect to the nature of the entering ligand lends also support to the trigonal bipyramidal intermediate on page 35.

5.2.6. *The role of the metal. Comparisons between Pt(II), Au(III) and Pd(II)*

The gold(III) and palladium(II) complexes are much more reactive than the corresponding platinum(II)-complexes. The relative reactivity $k_{\text{Au}}/k_{\text{Pt}}$ (Table I) depends strongly on the nature of the entering ligand. For the palladium(II) complexes the nature of the entering group seems to be of approximately the same importance as for the platinum(II) complexes.⁹⁰

In the platinum(II) reactions (12) and (13) studied in I, the solvent path is predominant. For the corresponding gold(III) reactions (IV) however, the contribution from the solvent path is small and substitution takes place mainly *via* a direct halide exchange. In fact, the relative contribution of the solvent path to the overall reaction is about 100-1000 times smaller in the case of gold for halide as entering ligand (IV).

For chloride as entering ligand the gold(III) complexes react about 10^5 times faster than the platinum(II) complexes and for bromide as entering ligand about 2×10^6 times faster. These observations support the picture of an associative intimate mechanism and are compatible with Baddley's and Basolo's⁹¹ conclusion

that bond formation in the transition state is more important for gold(III) than for platinum(II) complexes.

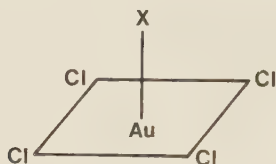
Finally, the relative *cis*-effect Cl^-/Br^- in the gold(III) system is 1.1 ± 0.1 (IV) and in the platinum(II) system 1.6 ± 0.2 . The relative *trans*-effects Br^-/Cl^- are 14 ± 3 for the gold(III) complexes and 6 ± 2 for the corresponding platinum(II) complexes. Thus, both the relative *cis*-effect and the relative *trans*-effect are of the same order of magnitude for the gold(III) and platinum(II) systems. It should be borne in mind, however, that *trans*-effects of ligands such as SCN^- , I^- , DMSO and C_2H_4 have not yet been quantitatively determined for gold(III) substrates. For the palladium(II) complexes studied in ref. 90 the relative *trans*-effects $\text{Cl}^-/\text{H}_2\text{O}$ and $\text{Br}^-/\text{H}_2\text{O}$ are about 6 times smaller than for platinum(II), whereas the *cis*-effects are a little higher. The experimental information for palladium(II) substrates is also rather incomplete, however.

5.3. Five-coordinate complexes

The rates of reaction of square-planar complexes are affected by the nature of the metal ion (cf. 5.2.6). The increase of reactivity is often explained by an increased ability to add a fifth ligand and evidence for five-coordinate intermediates of Ni(II) and Ir(I) are reported in the literature e.g. in the reactions of square-planar Ni(II)dithiolate complexes with dithiolate nucleophiles in aqueous solution where several five-coordinate intermediates were detected and their stabilities estimated.¹⁹ Other examples are the reactions of four- and five-coordinate complexes CODIr(Phen)X with ethylenediamine in aqueous solution where a stable five-coordinate intermediate CODIr(phen)(en)^+ has been detected in the substitution reaction of the four-coordinate system.²¹

Evidence for five-coordinate intermediates in ligand substitution reactions of gold(III) complexes, obtained from the kinetics has recently been reported by Hall and Satchell,²² who suggested ligand substitution in AuCl_4^- by bromide and thiocyanate to

proceed *via* formation of persistent five-coordinate intermediates of the type ($X=Br, SCN^-$).



This is not compatible with the present results (IV,V). Hall and Satchell's suggestion about the existence of persistent five-coordinate species in $AuCl_4^- - Br^-$ and $AuCl_4^- - SCN^-$ substitution reactions can be definitely disproved.

5.4. Conclusions

- Most of the kinetic evidence supports an associative mechanism *via* a trigonal-bipyramidal intermediate for both the k_1 -path and the k_2 -path. Grounds for this proposal can be summarized as follows:
 k_1 -path: i) its sensitivity to the nature of the solvent, which is the entering ligand in the rate-determining step of an associative mechanism (cf. Fig. 4b). ii) the rapid reactions of the solvento intermediates studied with the entering nucleophile Y. Intercepts in k_{exp} vs. $[Y]$ plots correspond to separately measured acid hydrolysis rate constants.
 k_2 -path: i) The effect of the nature of the entering ligand on both the relative *trans*-effect Cl^-/H_2O and the relative efficacy of H_2O and Cl^- as leaving ligands. ii) The independence of the relative *cis*-effect Cl^-/H_2O on the nature of the entering ligand.
- Available literature data and the present results give no support for an "unusual" behaviour of the k_1 -path. The present study shows that various rate equations can be derived from the general mechanisms (1) and (3) in paper III. Their mathematical form will depend on the experimental conditions used. The experimental rate equations reported so

far, are in accord with the general mechanisms. They give no support for any fundamental changes of mechanism.

3. The most important parameters for the substitution rates are the nature of the metal atom, the entering ligand and the *trans*-ligand. The nature of the *cis*-ligands and the ionic charge of the complex are of only minor importance.
4. The kinetics give no evidence for slow formation of long-lived five-coordinate intermediates as suggested for the ligand substitution in AuCl_4^- by bromide and thiocyanate.

6. REDUCTIVE ELIMINATION

Gold(III) complexes are easily reduced to gold(I) by ligands with reducing properties. Most redox reactions involving gold(III) complexes are reported to proceed by an initial substitution step followed by a rapid electron transfer which can be either an intramolecular⁹² process within the complex or an intermolecular^{93,94} reaction between the complex and an outer-sphere ligand. Bjerrum and Kirschner⁹⁵ found already in 1918 that tetrachloroaurate(III) dissolved in aqueous solutions of thiocyanate rapidly substitutes chloride by thiocyanate whereupon the tetrathio-cyanato aurate(III) is slowly reduced to gold(I) thiocyanato complexes.

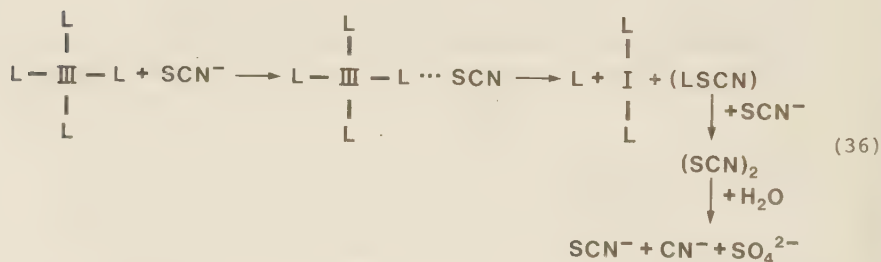
The kinetics for the overall reaction ($\text{L}=\text{Cl}, \text{Br}$ or SCN)



have been studied in V. The initial fast ligand substitutions have been described above (page 12). The rate of the subsequent redox process varies four orders of magnitude within the accessible concentration interval of gold. (V, Fig. 4). Bjerrum and Kirschner⁹⁵ were able to use sulfite titrations to follow the change of C_{Au} with time, whereas the experimental conditions in V gave stopped-flow rate. The redox process is first-order with respect to gold only for $C_{\text{Au}} < 10^{-5} \text{ M}$. The experiments indicate that the cyanide formed in the redox reaction inhibits the reaction, probably through for-

mation of gold(III)-cyanide complexes, which are reduced slowly. The observed gold(III)-dependence of the redox rate can be explained by this interaction between the cyanide ion formed and the unchanged gold(III).

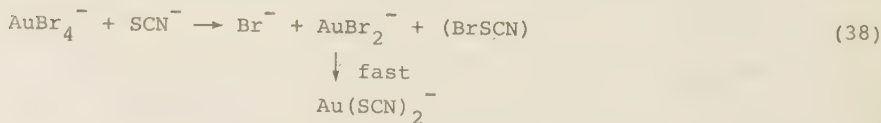
For moderately large concentrations of thiocyanate ($[\text{SCN}^-] \leq 5\text{mM}$) the rate of reduction is proportional to $[\text{SCN}^-]$ for constant ratios $[\text{SCN}^-]/[\text{X}^-]$, which indicates an intermolecular reaction *via* an attack on the complex by an outer-sphere thiocyanate in accordance with the following intimate mechanism:



The experiments indicate that each complex $\text{AuX}_{4-n}(\text{SCN})_n^-$, $n=0,1,2,3,4$ can be reduced. The observed redox rate constants are in principle sums of rate constants for the parallel paths of the mechanism in Figure 2 on page 12 and can not be resolved. The reduction rate constant for the process



can be determined independently, however, as $k_{r4} = (2.4 \pm 0.2) \times 10^3 \text{M}^{-1} \text{s}^{-1}$ and by extrapolation the reduction rate constant for the process



can be obtained as $k_{r0} = (5 \pm 1) \times 10^4 \text{M}^{-1} \text{s}^{-1}$. The reverse reaction is negligible. The explanation might be either that the equilibrium



where L = Cl, Br or SCN is displaced towards the Au(I), which is valid for the reaction $\text{AuI}_4^- \rightleftharpoons \text{AuI}_2^- + \text{I}_2$ ⁹⁶ or that the formed species (LSCN) is rapidly decomposed by water.⁹⁷⁻⁹⁹ All attempts to detect (SCN)₂ or (LSCN) species in aqueous solutions using stopped-flow techniques have failed.

Hall and Satchell²² also observed two reactions in the stopped-flow region when thiocyanate was added to solutions of tetrachloroaurate(III) but considered the possibility that the subsequent reaction was due to a reduction of Au(III) to Au(I) less probable since the earlier studies had shown the reduction to be relatively slow.^{95,100} They overlooked the fact that high concentrations of Au(III) had been used in these earlier studies and that the reduction rate is strongly dependent on the Au(III) concentration (V, Fig. 4).

For $[\text{SCN}^-] \leq 5\text{mM}$ there is a linear relationship between the reduction rate and the thiocyanate concentration. For higher concentrations deviations are observed (V, Fig. 5). The reasons for these deviations are not quite clear at present. One explanation might be that higher thiocyanato complexes are formed. Already Bjerrum and Kirschner⁹⁵ suggested the existence of $\text{Au}(\text{SCN})_5^{2-}$ and $\text{Au}(\text{SCN})_6^{3-}$ for $[\text{SCN}^-] \geq 200\text{mM}$. There are many examples of stable six-coordinate gold(III) complexes with a distorted octahedral structure.¹⁰¹⁻¹⁰³ The mechanism for the redox process in this interval of thiocyanate concentration needs further study (cf. V).

7. SPECTRA

The charge-transfer spectra of the complexes MCl_4^{j-} , MBr_4^{j-} and $\text{M}(\text{SCN})_4^{j-}$, M=Pt, Pd and Au are shown in Fig. 5 and suggested assignments are given in Table IV. The bands are displaced towards the visible spectral region when the ligand is changed from Cl^- to Br^- to SCN^- for all three metal ions. Elding and Olsson¹⁰⁴ have discussed the spectra of MX_4^{2-} , M=Pt and Pd, X=Cl and Br. No splitting of the bands at $3.37 \mu\text{m}^{-1}$ and $3.73 \mu\text{m}^{-1}$ due to spin-orbit coupling like that found for the band at $4.05 \mu\text{m}^{-1}$ of

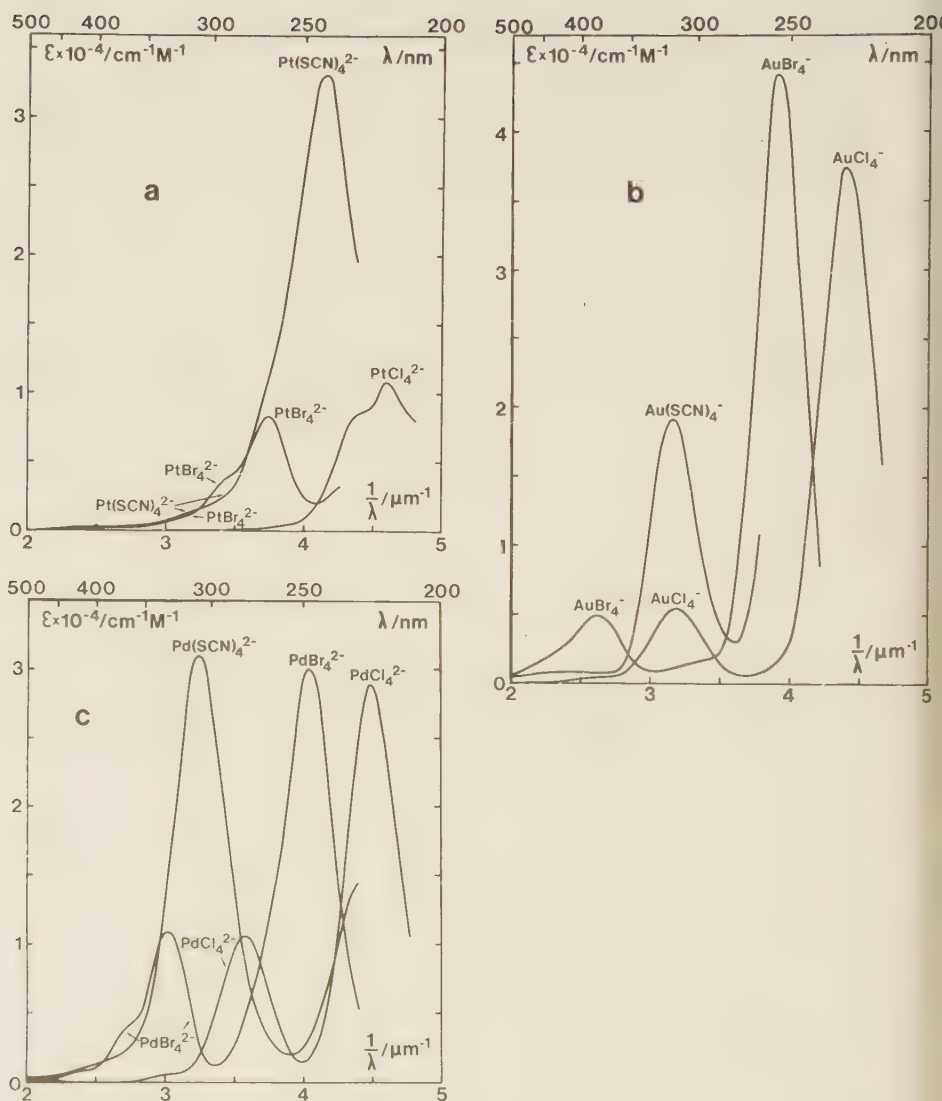


Figure 5. Charge transfer spectra for a) PtX_4^{2-} b) AuX_4^- and c) PdX_4^{2-} , $\text{X}=\text{Cl}, \text{Br}$ and SCN .

PdBr_4^{2-} can be observed for PtBr_4^{2-} . The spectra of the gold complexes are very similar to those of palladium(II).

Table IV. Wavenumbers, $\lambda^{-1}/\mu\text{m}^{-1}$ and Molar Absorptivities $\epsilon_M/\text{cm}^{-1}\text{M}^{-1}$ for MX_4^{j-} , $\text{M}=\text{Pt}$, Pd and Au and $\text{X}=\text{Cl}$, Br and SCN . ($j=1$ for $\text{M}=\text{Au}$ and 2 for $\text{M}=\text{Pt}$, Pd)

	$\text{M} = \text{Pt}^a$	$\text{M} = \text{Pd}^{a,b}$	$\text{M} = \text{Au}$
Assignment	$3a_{1g} \rightarrow 2a_{2u}$	$3b_{1g} \rightarrow 2e_u$	$3b_{1g} \rightarrow 2e_u$
MCl_4^-	4.61(10800)	4.50(29000)	4.39(37500)
MBr_4^-	3.73(8300)	4.05(30000)	3.92(44000)
MSCN_4^-	?	3.25(31300)	3.10(19200)

a Ref. 104. b Ref. 105.

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